Safety of Reactive Chemicals and Pyrotechnics

Tadao Yoshida
Yuji Wada
Natalie Foster

Industrial Safety Series

Volume 5

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Industrial Safety Series, 5

Safety of Reactive Chemicals and Pyrotechnics

by

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Preface

The authors of this book also published "Safety of Reactive Chemicals," in which excellent, practical methods for testing chemicals were introduced. These methods were selected from those used in various countries.

In the previous volume, the authors and their collaborators examined and improved these existing methods and developed additional new ones. Recently, the Japanese Fire Services Law was amended, and under this law hazardous materials were required to be evaluated and classified by appropriate tests.

Considering these developments, we decided to introduce in this book primarily new testing methods that were not discussed in "Safety of Reactive Chemicals." As was the case with our first volume, this book is also intended to be easily understood.

This English version is the translation of the orignal Japanese book which was published by the Taisei Publishing Company Limited in 1988. In making this English version, we asked many people to cooperate with us. In developing new testing methods, the assistance of students in Yoshida Laboratory and associate fellows -- Kotaro Muranaga, Masatoshi Watanabe, Yoshiaki Kaneko, Yoshimasa Inoue, Noriaki Tanaka and Toshio Matsuzawa -- was indispensable. The Japan Carlit Co., Ltd., Nippon Oil & Fats Co., Ltd. and Nippon Kayaku Co., Ltd. allowed us to use their facilities for experiments. In studying the safety of pyrotechnics, we cooperated with Terumitsu Saito, Naota Kobayashi and Eishi Kuroda, and were allowed to use the facility of Nippon Koki Co., Ltd. We thank all people and companies who helped us.

For the production of this publication, we received assistance from many companies listed among the contributors to this edition for making an English draft of the edition. For the completion of the English version, Dr. Natalie Foster followed by Dr. Bruce Thomson provided editorial assistance. We express our gratitude to them. Miss Sanae Watanabe and Mr. Yuji Wada, Jinhua Peng and Yuhua Yu contributed greatly to the editing of these books. The authors would like to express their appreciation for these services.

Tadao Yoshida
Sepember 1994

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Chapter 1

REACTIVE CHEMICALS AND THE EVALUATION OF THEIR HAZARDS

1.1 Introduction

Numerous chemical substances are distributed in normal commerce and many new ones are introduced every year. Some of these substances have the potential to cause environmental problems, affect health adversely, or to cause fires or explosions. These chemicals are regulated as hazardous materials and are handled with appropriate care to minimize accidents.

The category "hazardous materials" includes a group of chemical substances called "reactive chemicals". A reactive chemical initiates reaction by itself or with other substances. These reactions are often exothermic (heat releasing) or produce flammable gases or explosive materials, which may in turn trigger accidents.

The purposes of this book are :

1. To introduce methods for the evaluation of the hazards of reactive chemicals relating to fires and explosions. Evaluation methods have been studied in a number of countries and certain achievements have been published 1) 2) . In 1982, one of the authors (Yoshida) published "Safety of Reactive Chemicals" 3) , introducing evaluation methods which had been subjected to worldwide scrutiny. This book aims to introduce the most practical evaluation methods available at the present time, specifically including ones developed after the publication of "Safety of Reactive Chemicals". The methods already described in "Safety of Reactive Chemicals" are referenced in this book without regard to their relative importance.
2. To enable those who cannot directly conduct appropriate tests to understand necessary methodology so that they can successfully subcontract required evaluations to outside professional institutions. By doing so, it is expected that use of highly hazardous reactive chemicals can be decreased and reactive chemicals can be used under safer conditions.
3. To educate people who handle chemicals to minimize the potential of possible accidents. Many accidents caused by reactive chemicals could have been prevented if people had sufficient knowledge of the hazards associated with reactive chemicals. By

means of this book, we hope to provide handlers of chemicals with such information.

4. To present methods for the evaluation of the safety of pyrotechnics. Pyrotechnics are devices which generate heat, gas, flame, sound, light, or smoke, and thereby provide valuable functions. Because of their behavior -- because they generate heat, gas, flame, sound, light or smoke -- they are by definition hazardous. Pyrotechnics are employed in, among other items, rockets, fireworks, air bags, the tensioners of seat belts, life-saving signals, smoke tubes for signaling, and disposable pocket heaters. Generally the safe handling of reactive chemicals improves if they are moulded or pressed as is usual in case of pyrotechnics. We hope that readers will understand the relationships between safe handling and appropriate packaging and will use this book as a guide to develop increasingly safe pyrotechnic devices, which are expected to become even more popular in the future.

This book consists of five chapters. Readers may start in any part depending upon their needs and interests.

Chapter 1 : As an introduction, Chapter 1 describes the purposes of the book, its contents, explanations of technical terms, and outlines of evaluation methods for hazardous materials and reactive chemicals.

Chapter 2 : Typical examples of accidents involving reactive chemicals are presented so that readers will understand the nature of existing hazards associated with reactive chemicals. Readers will appreciate that similar accidents can happen in the future and that countermeasures should be prepared to prevent such accidents.

Chapter 3 : This chapter begins with descriptions of typical screening tests such as the ignitability test, differential scanning calorimetry (DSC) and the drop ball test. Firms and laboratories which frequently develop new reactive chemicals should be equipped with appropriate facilities to carry out these screening tests. A screening test is safe, simple and gives quite useful information. In situations where large quantities of reactive chemicals are used, it is necessary to conduct several standard tests in parallel to estimate with high reliability the hazards associated with a particular substance.

In the latter half of Chapter 3, standard testing methods are introduced which are applicable to the evaluation of self-reactive substances. As stated previously, methods already known and described in "Safety of Reactive Chemicals" 3) are briefly mentioned. Primarily methods developed after the publication of "Safety of Reactive Chemicals" are explained in this book, and all the methods 26) adopted under the Japanese Fire Services Law are described.

Chapter 4 : Examples of combined testing methods for the evaluation of certain hazardous substances are described. In the case of substances whose methods of handling are restricted by law, every evaluation method stipulated in the law is mentioned in this book.

Chapter 5 : Chapters 1 through 5 introduce evaluation methods for reactive chemicals and hazardous materials themselves. Chapter 5 includes discussions of products called pyrotechnics, which utilize properties of reactive chemicals to provide useful and desired effects. This category of products is expected to be further developed in the future. Generally, pyrotechnics themselves are less hazardous than the substances from which they are manufactured. Pyrotechnic devices can be made safe if the items are carefully designed and manufactured with due attention to the potential hazards of the components. Examples of evaluations of the safety of pyrotechnics from the authors' personal experiences are included.

1.2 Chemical Substances, Hazardous Materials, Reactive Chemicals and Pyrotechnics

1.2.1 Chemical substances

Chemical substances are materials which can be produced or used in chemical processes. Chemical processes include such reactions as combustion. Since the rise of the modern chemical industry in the nineteenth century, numerous chemical substances have been developed and created including acids, bases, fertilizers, ceramics, catalysts, dyestuffs, fabrics, explosives, paints, plastics, petrochemicals, pharmaceuticals, agricultural chemicals, specialty chemicals, automotive materials, and home and commercial electronics components.

1.2.2 Hazardous materials

Chemical substances which may cause adverse effects to human health, endanger people's lives or damage the environment are called hazardous materials. In Japan, hazardous materials are distinguished by two general legal definitions : namely, hazardous chemicals in a narrow sense and hazardous materials in a broad sense.

Hazardous chemicals in a narrow sense are those substances having ignitability and flammability as specified in the Japanese Fire Services Law; these materials are listed in the Exhibit of the Law.

The Fire Services Law was revised in May, 1988, and the listing of hazardous materials has been also revised as shown in Table 1.1. The new definition of hazardous materials under the revised Fire Services Law employs modern classification methods utilizing special evaluation techniques. The following quotation comes from the official gazette and demonstrates the principle of the revision 25) .

Hazardous materials in the broad sense are materials having hazards such as combustibility, explosiveness, corrosiveness and toxicity. The concept is represented by the United Nations' Recommendation on the Transport of Dangerous Goods. This classification has been adopted with almost no change in the IMDG-Code and

Ministerial Ordinance for Material Transportation and Storage of Hazardous Substance of the Ministry of Transportation. The hazardous material classification by the United Nations is shown in Table 1.2.

The classification by the United Nations consists of nine classes. Some classes are further broken down into divisions.

Furthermore, the classification by the United Nations applies only to materials to be transported. Some hazardous materials are not covered by these classification. For example, materials regulated to prevent environmental pollution are not stipulated in these classifications.

In Japan, in addition to the Fire Services Law, there are the Explosives Control Law (governing explosive materials), the High Pressure Gas Control Law (regulating high pressure gases), the law concerning the Prevention of Hazards of Radioisotopes, the Poisonous and Deleterious Substances Control Law (concerning toxic and deleterios substances) and regulations for environmental controls, each instituted because of concerns for hazardous materials in different administrative fields.

Law for Amendment of Fire Services Law (Law No.55)
(Ministry of Home Affairs)
1. Scope of hazardous materials
(1) Clarifying the definition of hazardous materials and introducing a system of judging hazards by tests (Article 2 and Exhibit).
(a) Hazards of First Group Hazardous Materials (oxidizing solids) are judged by two tests to evaluate potential hazards of oxidation and impact sensitivity.
(b) Hazards of Second Group Hazardous Materials (flammable solids) are judged, in principle, by the tests to examine ignitability and flammability by flame.
(c) Hazards of Third Group Hazardous Materials (spontaneously combustible materials and water-reactive substances) are judged, in principle, by the tests to evaluate combustibility in the air, and combustibility or the possibility of generating flammable gas in case of contact with water.
(d) Hazards of Fourth Group Hazardous Materials (flammable liquids) are judged, in principle, by the tests to examine flammability.
(e) Hazards of Fifth Group Hazardous Materials (self-reactive substances) are judged, in principle, by the tests to evaluate explosivity and violence of exothermic decomposition.
(f) Hazards of Sixth Group Hazardous Materials (oxidizing liquids) are judged by a test to evaluate potential oxidizing hazards.

Table 1.1 Exhibit of hazardous materials under the revised Fire Services Law (Art. 2, Art. 10 and Art. 11-4)

Group	Property	Item
First	Oxidizing solids	1. Chlorates 2. Perchlorates 3. Inorganic peroxides 4. Chlorites 5. Bromates 6. Nitrates 7. Iodates 8. Permanganates 9. Dichromates 10. Other materials specified by Cabinet Order 11. Materials containing one of the materials described in the above items 1-10
Second	Flammable solids	1. Phosphorus sulfide 2. Red phosphorus 3. Sulfur 4. Iron powder 5. Metal powders 6. Magnesium 7. Other materials specified by Cabinet Order 8. Materials containing one of the materials described in the obove item 1-7 9. Flammable solids
Third	Spontaneously combustible materials and water reactive substances	1. Potassium 2. Sodium 3. Alkyl aluminium compounds 4. Alkyl lithium compounds 5. White phosphorus 6. Alkali metals (except for potassium and sodium) and alkaline earth metals 7. Organometallic compounds (except for alkyl aluminium and alkyl lithium compounds) 8. Hydrides of metals 9. Phosphides of metals

		10. Carbides of calcium and aluminium 11. Other materials specified by Cabinet Order 12. Materials containing one of the materials described in the above items 1-11
Fourth	Flammable liquids	1. Special flammable materials 2. First class petroleum substances 3. Alcohols 4. Second class petroleum substances 5. Third class petroleum substances 6. Fourth class petroleum substances 7. Animal / vegetable oils
Fifth	Self-reactive substances	1. Organic peroxides 2. Nitrate esters 3. Nitro compounds 4. Nitroso compounds 5. Azo compounds 6. Diazo compounds 7. Derivatives of hydrazine 8. Other materials specified by Cabinet Order 9. Materials containing one of the materials described in the above items 1-8
Sixth	Oxidizing liquids	1. Perchloric acid 2. Hydrogen peroxide 3. Nitric acid 4. Other materials specified by Cabinet Order 5. Materials containing one of the materials described in the above items 1-4

Table 1.2 The U.N. classification of hazardous materials

Class	Devision	Definition
1. Explosive	1.1	Substances and articles which have a mass explosion hazard.
	1.2	Substances and articles which have a projection hazard but not a mass explosion hazard.
	1.3	Substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard.
	1.4	Substances and articles which present no significant hazard.
	1.5	Very insensitive substances which have a mass explosion hazard
	1.6	Extremely insensitive articles which do not have a mass explosion hazard
2. Gases		Gases compressed, liqufied, dissolved, under pressure or refrigerated.
3. Flammable liquids		Liquid, or mixtures of liquids, or liquids containing solids in solution or suspension which give off a flammable vapor at temperatures of not more than 60.5°C, closed-cup test, or not more than 65.6°C, open-cup test.
4. Flammable solids	4.1 Flammable solids	Solids, other than those classed as explosives, which under conditions encountered in transport are readily combustible, or may cause or contribute to fire through friction.
	4.2 Substances liable to spontaneous combustion	Substances which are liable to sponaneous heating under normal condition encountered in transport, or to heating up in contact with air, and

		being then liable to catch fire.
	4.3 Substances which, in contact with water, emit flammable gases	Substances which, by interaction with water, are liable to became spontaneously flammable or to give off flammable gases in dangerous quantities.
5. Oxidizing substances and Organic peroxides	5.1 Oxidizing substances	Substances which, while in themselves not necessarily combustible, may generally by yielding oxygen, cause or contribute to, the combustion of other material.
	5.2 Organic peroxides	Organic substances which contain the bivalent -0-0- structure and may be considered derivatives of hydorogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals. Organic peroxides are thermally unstable substances which may undergo exothermic self-accelerating decomposition.
6. Poisonous (toxic) and infectious substances	6.1 Poisonous (toxic) substances	Substances liable either to cause death or serious injury or to harm human health if swallowed or inhaled or by skin contact.
	6.2 Infectious substances	Substances containing viable micro-organisms or their toxins which are known, or suspected, to cause disease in animals or humans.
7. Radioactive materials		Materials for which the specific activity is greater than 70kBq/kg(0.002<μCi /g).
8. Corrosives		Substances which, by chemical action, will cause severe damage when in contact with living tissue, or, in case of leakage, will materially damage, or even destroy, other goods or the means of transport.
9. Miscellaneous danger-substances		Substances and articles which during transport present a danger not covered by other classes.

To secure the safety and hygiene of workers, Japan has the Labor Safety and Sanitation Law, which regulates harmful and hazardous materials to prevent labor−related accidents.

In 1971, the Occupational Safety and Health Agency (OSHA), under the control of Department of Labor of the U.S. Government, introduced a definition of hazardous materials in its regulation for labor as follows :

"Hazardous materials" means substances which have one or more special characteristics as listed below :

(1) Flash point of 140 ° F or lower in the closed−cup test method, or easy, spontaneous thermal reaction.
(2) Allowable concentration of 500ppm or less as gas or vapour, 500mg/m ^{3} or less as haze, and 25mppcf or less(1mppcf = 1 million particles per 1ft ^{3}) as dust.
(3) Oral LD_{50} dosage of 50mg/kg or less.
(4) Polymerization causing radical exothermic reaction.
(5) Strong oxidizing or reducing property.
(6) Strong first−class burn with short−time exposure, or causing injury by skin contact.
(7) Generation of dust, gas, mist, vapour, fog or smoke having one or more characteristics of items (1)−(6) stipulated above under ordinary operation.

1.2.3 Reactive chemicals

A reactive chemical is a substance which may cause fire or explosion by reacting with itself or with other substances. Reactive chemicals are divided into two categories: self−reactive substances and reactive substances with other materials.

Self−reactive substances are those which can initiate exothermic decomposition without reacting with oxygen in the air, causing rapid gas generation and deflagration leading to combustion or explosion. Self−reactive substances are occasionally called unstable substances because many of them experience thermal decomposition at a relatively low temperature. Recently the term "self−reactive substance" has been used as an official term both in Japan and abroad.

Self−reactive substances have caused some well−known accidents in the past [4]. Even today it is not difficult to find references to such accidents. However, because the number of accidents has not been large, these accidents have not attracted public attention. Currently increasing is the number of cases in which results are more devastating than expected, although the accidents themselves do not seem serious. It is becoming increasingly important to avoid accidents by evaluating potential hazards of self−reactive substances and to establish methods to handle those materials safely in accordance with their properties.

1.2.4 Pyrotechnics

The term "pyrotechnics" is defined in the Explosive Control Law in Japan as those items manufactured with propellants or explosives to meet a certain purpose 5) . The materials having pyrotechnical effects are called pyrotechnics in general. Pyrotechnical effects refer to the emission of heat, light, flame, sound, gas or smoke. The terms "pyrotechnic compositions" or "pyrotechnic mixtures" are broadly used. These terms refer to the raw materials for the production of pyrotechnics. Recommendations on the Transport of Dangerous Goods of United Nations 6) defines "pyrotechnic substance" as follows :

"A pyrotechnic substance is a substance or a mixture of substances designed to produce an effect by heat, light, sound, gas and smoke, or a combination of these as the result of non-detonative self-sustaining exothermic chemical reactions."

The term "pyrotechnics" in English also means the technology of pyrotechnics and is defined as "technology to utilize chemically-generated light, heat or sound for amusement, utility or warfare" 7) .

Pyrotechnic compositions or mixtures, which are usually combinations of oxidizing and combustible materials, generate heat when they react. The material or mixture which generates a large amount of heat through such reaction is called an "energetic material" or an "energetic mixture".

1.3 Definition of Hazardous Materials and Their Evaluation Methods

There are three main categories of hazards : namely, fire and explosion hazards, health hazards and environmental hazards. Different evaluation methods exist for each category. Not being experts in every evaluation method, the authors will refer only to the evaluation methods which are generally used. Evaluation methods according to the U.N. classification system, which covers a wide range of hazardous materials, are explained.

1.3.1 Explosive substances (Self-reactive substances and products which contain self-reactive substances and may explode)

Explosive substances should be evaluated in terms of possibility, ease and violence of explosion: in other words, in terms of their ability to propagate an explosion, their sensitivity and their power. Specific evaluation methods are explained in Paragraph 1.4 and Chapter 3.

1.3.2 High pressure gas

Hazards associated with gases under high pressure consist mainly of toxicity, flammability, spontaneous combustibility, explosiveness, the ability to support combustion, and bursting of their container.

As an index for toxicity of gaseous substances, the median lethal concentration (LC_{50}) and the threshold limit value (TLV) are used to evaluate acute toxicity. LC_{50} is the gas concentration (ppm) in air which results in the death of 50% of a population of test animals by inhalation. TLV is the threshold limit of exposure which does not cause any serious sickness in workers under normal conditions of an 8 hours day and a 40–48 hour work week. TLV is usually given in combination with the time–weighted–average concentrations for 8 hours per day (TLV–TWA), or with the short time exposure limit (TLV–STEL), which is that exposure which should not be exceeded even for a relatively short period (15–30 minutes), or with the ultimate limit (TLV–C), which defines the exposure level that should not be exceeded under any circumstances.

As an index for gas flammability, the flammable range (lower flammability limit (LFL) and upper flammability limit (UFL)) and the minimum ignition energy (MIE) are often used. When a flammable gas or vapor of a flammable liquid is mixed with air or an oxidizing gas in a certain ratio and is ignited, the gas mixture burns or explodes. The range of values of the ratios of fuel to oxidizer over which combustion or explosion can be supported is called the flammable range. The lower limit of this ratio at which a flammable material will burn is called the lower flammability limit and the upper limit is called the upper flammability limit; the lower and upper limits of the ratio at which the mixture eyplodes are called respectively the lower explotion limit (LEL) and the upper exprosion limit (UEL).

The minimum ignition energy is simply the minimum energy necessary to cause the ignition of a mixture of flammable gas and oxidizing gas within the flammable range. It is usually measured by an electrical spark discharge because of the ease of the test.

Two conditions can give rise to the spontaneous combustion of a fuel. One condition involves contact of the material with air. The other is the spontaneous ignition of an unstable self–reactive substance when it is kept at a sufficiently high temperature. Silane (SiH_4) and phosphine (PH_3) are the examples of the former case, and a mixed atmosphere of air and nickel carbonyl($Ni(CO)_4$) or carbon disulfide (CS_2) are examples of the latter.

The ignition point (or auto–ignition point) is used as an index of the spontaneous combustibility of a flammable gas in air. The ignition point is the lowest temperature at which ignition can occur by heating a flammable gas in an atmosphere which will support combustion in the absence of an ignition source such as a flame or electric spark.

Some gases explode by themselves without being mixed with other gases. For example, acetylene, ethylene oxide and ozone fall into this category. This property is recognized experimentally and no common evaluation method has been established. If the calculated decomposition heat of 1g of the gas is large, it is assumed that the material may induce a decomposition explosion.

Combustion supporting gases include air, oxygen, ozone and carbon monoxide. General evaluation methods for the ability of a gas to support combustion have not been established. When a gas is compressed, it becomes likely to burst its container, but general evaluation methods for bursting have not been established. The bursting depends on characteristics of the vessel in which the gas is stored rather than on the characteristics of the gas itself.

There are several other forms of matter having characteristics similar to gases, such as vapour, mist, dust, fume, and smoke. These materials are classified in Table 1.3.

Table 1.3 Properties of harmful materials in air

Kind	Property	Particle diameter[μm]
Gas	Gas phase at 25°C and 760mmHg	Molecule
Vapor	Gas generated from the surface of a solid or a liquid under 25°C and 760mmHg	Molecule
Mist	Fine particles of liquid dispersed in air	0.1-100
Dust	Fine particles of solid dispersed in air	0.1-100
Fume	Fine particles of compounds derived from inorganic gas or metal vapor by chemical reaction	0.1-1
Smoke	Fine perticles generated by incomplete combustion of organic materials	0.1-1

1.3.3 Flammable liquids

Ignition refers to the phenomenon occurring when the vapor arising from a flammable liquid begins to burn when an ignition source is introduced into the air space above the surface of the liquid. The lowest temperature at which ignition occurs is called the flash point. At the flash point, vapor concentration near surface of a flammable liquid is equal to the concentration defined by the lower flammability limit.

As an index of the hazards of a flammable liquid, the flash point and the ignition point are used. Various evaluation methods exist to determine the flash point. Results of tests conducted with a closed–cup flash point apparatus are usually used as the flash point. Liquids with low ignition points are regarded as highly dangerous because they ignite easily and usually burn more fiereely than liquids with high ignition points.

1.3.4 Flammable solids

1.3.4.1 Flammable solids

The U.N. classification scheme defines flammable solids as solids, other than those classed as explosives, which under conditions encountered in transport are readily combustible, or may cause or contribute to fire through friction. The category includes self–reactive substances and wetted explosives.

On the other hand, the Japanese Fire Services Law defines flammable solids as solids which tend to burn easily in the air, excluding self–reactive substances.

Generally ignitability and burning rate are used as indices of hazards of solids combustible in the air. The ignitability is judged by the following "small gas–flame ignitability test":

(1) Contact a small gas–flame to a solid material for 10 seconds to ignite it.

(2) Examine whether the solid material continues to burn.

The burning rate is measured by the following methods. :

(1) Under given conditions, ignite a sample and measure the time required for the sample to completely burn off (U.N. burning rate test/the burning rate test in the Japanese Fire Services Law).

(2) Measure the time required for a sample of 10 cm to completely burn off (burning rate test proposed in U. K.).

(3) Under airtight conditions, ignite a sample and measure the time required for the pressure to reach some other given level (time pressure test).

1.3.4.2 Spontaneously combustible substances

The U.N. classification scheme defines spontaneously combustible substances as substances which are liable to heat spontaneously under normal conditions encountered in transport, or to heat up in contact with air and then to catch fire.

The spontaneous combustibility described above is judged by the following tests. :

(1) SADT (self–accelerating decomposition temperature) measured by the Heat Accumulation Storage Test.

(2) Spontaneous combustibility measured by heating a sample in contact with air

(IMO test, CFR test, etc.).

(3) Spontaneous combustibility in contact with air under room temperature (Japanese Fire Services Law).

(4) Decomposition on-set temperature (TDSC, TDTA) measured through thermal analysis.

1.3.4.3 Water-reactive substances

The U.N. classification scheme defines water-reactive substances as substances which are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities by interaction with water. Water-reactive substances include, among others, alkaline metals (Na, K, Li, etc.), hydrogenates, and organometallic compounds.

Their hazards are evaluated by the amount of flammable gas generated when a sample is put into water (U.N. Recommendation, Japanese Fire Services Law).

1.3.5 Oxidizing substances and Organic peroxides

1.3.5.1 Oxidizing substances

The U.N. classification defines oxidizing substances as substances which, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause or contribute to the combustion of other materials 6).

Hazardous properties of oxidizing materials are as follows :

(1) hazardous flammability and explosiveness when mixed with combustible materials,

(2) in some cases explosiveness of an oxidizer itself,

(3) hypergolic ignition hazards, and

(4) toxicity.

Oxidizers which themselves tend to explode include, among others, ammonium chlorate, ammonium perchlorate, ammonium nitrate, and silver chlorate. These explosive oxidizers can be evaluated by the test methods for explosive substances. Their toxicity is evaluated based on their LD_{50} (lethal median dose) values. LD_{50} (mg/kg) means a dose killing 50% of test animals, which is converted into a dose per 1 kg of body weight. When mixed with other combustible substances, the oxidizers exhibit hazardous flammability and explosiveness. The flammability is evaluated by combustion of a mixture of an oxidizer with wood meal (U.N. Recommendation, Japanese Fire Services Law). The shorter the combustion time, the greater the flammability hazard of the oxidizer. On the other hand, the explosiveness is evaluated by the drop ball test using a mixture of an oxidizer with red phosphorous (Japanese Fire Services Law). In this test, an oxidizer that ignites at a low impact energy is considered to have a greater explosion hazard than one which ignites at a higher impact energy.

Some oxidizers tend to ignite when mixed or put in contact with acids or organic materials (hypergolic ignition). Hypergolic ignition can contribute to fires caused in chemical laboratories during earthquakes. The hypergolic ignition hazard is evaluated using the hypergolic ignition tester, which examines whether an oxidizer ignites when mixed with two kinds of chemicals (modified steel–dish test).

Though most oxidizing substances are solid, there are some liquid ones. The Japanese Fire Services Law regulates liquid oxidizing substances as the 6th Group of Hazardous Materials. Hazards of a liquid oxidizer are evaluated by the following methods (Japanese Fire Services Law, U.N. Recommendation) :

(1) sprinkle the liquid oxidizer on wood meal, and
(2) ignite the wood meal and examine whether it burns or not.

1.3.5.2 Organic peroxides (self–reactive substances)

The U.N. Recommendations defines organic peroxide as organic substances which contain the bivalent "–O–O–" structure and may be considered derivatives of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals.

Organic peroxides are thermally unstable substances which may undergo exothermic self–accelerating decomposition. The Japanese Fire Services Law has revised its classification to regulate organic peroxides as self–reactive substances.

Among the hazardous properties of self–reactive substances including organic peroxides are explosiveness, violent deflagration, self–accelerating exothermic decomposition, instability, hypergolic ignition, flammability, corrosiveness and toxicity. Evaluation methods for these hazardous properties are described in Paragraph 1.4 and Chapter 3.

1.3.6 Toxic substances

1.3.6.1 Toxic substances

The U.N. Recommendations define toxic substances as substances liable either to cause death or serious injury or to harm human health if swallowed or inhaled or brought into contact with the skin [6] . Indices of hazardous properties of toxic substances include carcinogenicity and mutagenicity as well as LC_{50}, LD_{50} and TLV. All TLV based values listed in Sect. 1.3.2 are implied here. In Japan, these toxic substances are regulated by the Toxic and Deleterious Substances Control Law.

1.3.6.2 Infectious substances

The U.N. Recommendations define infectious substances as substances containing viable micro–organisms or their toxins which are known, or suspected, to cause disease in animals or humans [6] . Evaluation methods for assessing the hazards associated with infectious substances are beyond the scope of this book. The interested reader should consult other technical books specializing in that subject.

1.3.6.3 Radioactive materials

The U.N. Recommendations define radioactive materials as materials for which the specific activity is greater than 0.002<Ci/g. Exposure to radioactivity causes physical difficulties and may influence the integrity of genetic information. With respect to evaluation methods for these substances, which are beyond the scope of this book, the interested reader should refer to technical books specializing in the subject.

1.3.7 Corrosive substances

The U.N. Recommendations define corrosive substances as substances which, by chemical reaction, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport[6]. With respect to evaluation methods for these substances, please refer to technical books specializing in the subject.

1.3.8 Other hazardous substances

Hazardous substances other than those classified above fall within this group.

1.3.9 Dust, mist and vapor

These are not regulated as hazardous substance, since they are not considered to be generated in large quantities in the course of transportation. In manufacturing processes and during handling other than transport, they are sometimes generated to a hazardous extent and cause accidents. The main hazards with dust from a combustible material is its tendency to explode violently when mixed with air and ignited. This hazardous property is evaluated by measuring minimum ignition energy, lower flammability limit and explosive pressure rate, all of which may be measured using a dust explosion measuring apparatus.

1.4 Reactive Chemicals and The Evaluation of Their Hazards

1.4.1 Hazards of chemicals

Phenomena relating to the hazards of reactive chemicals include detonation (a violent explosion with an accompanying shock wave), deflagration (the movement of an exothermic reaction zone without accompanying shock waves and not consuming oxygen from the air), thermal explosion (a rapid self–accelerating exothermic reaction occurring when a system's heat generation exceeds its heat loss), and hypergolic ignition or hypergolic exothermic reaction. For each of these phenomena, the probability of occurrence, ease of occurrence, magnitude, and violence will be discussed. Different testing methods are used to measure each feature. Table 1.4 shows the relationships among these indices and is helpful to tell what aspect of a hazard a test evaluates.

TABLE 1.4 Hazardous phenomena and types of hazards

Phenomenon	Types of hazards			
	Proba-bility	Ease of occurrence	Magnitude of occurrence	Violence
Detonation				
Deflagration				
Thermal explosion				
Hypergolic reaction				

There are two ways to tell the probability of the occurrence of hazardous phenomenon. One is to see whether an exothermic reaction is involved. This is relatively simple and the likelihood can be estimated by looking at the structural formula, by calculating the heat of reaction, or by thermal analysis. The other way is to determine whether a substance can sustain an exothermic reaction if an exothermic reaction occurs. The ability to sustain an exotherm is rather difficult to prove with a smallscale experiment. For example, it is known that in detonation a substance tends to propagate a reaction more easily if the sample has a larger diameter and more unevenness, and if the experiment is conducted in a space sealed more tightly and at a higher temperature. An experiment to prove that propagation does not take place is very useful for the assessment of safety. As some measures such as dilution can decrease the hazard associated with a substance, it is very important to conduct a test for the ability to propagate explosion that is highly reliable.

For substances found to participate in exothermic reactions, an experiment is necessary to establish the ease of initiation of such a reaction. For example, ease of detonation can be tested by mechanical stimulation, such as a blow or friction, or by detonation impulse such as a shock wave. Generally a mechanical stimulation gives a weak impact, and a strong impact is given by a detonation impulse or from a rapid flying piece of material expelled during an explosion.

Substances which explode by a weak impact (called highly sensitive substances) can be identified by a screening test like the drop ball test. Whether deflagration occurs easily can be checked by an ignitability test. Another screening test to examine the ease of occurrence of a reaction relies on the determination of the temperature at which decomposition is initiated by thermal analysis on micro-samples. This quantifies the ease of initiating a thermal explosion.

Substances which react easily in the above tests should be regarded as materials which require considerable caution in handling. They should be used only if appropriate safety precautions may be taken.

The magnitude of the reaction is an index of the potential of a hazard. The screening tests for the magnitude of a reaction include reaction heat calculation, reaction calorimetry and sealed cell differential scanning scanning calorimetry (SC-DSC).

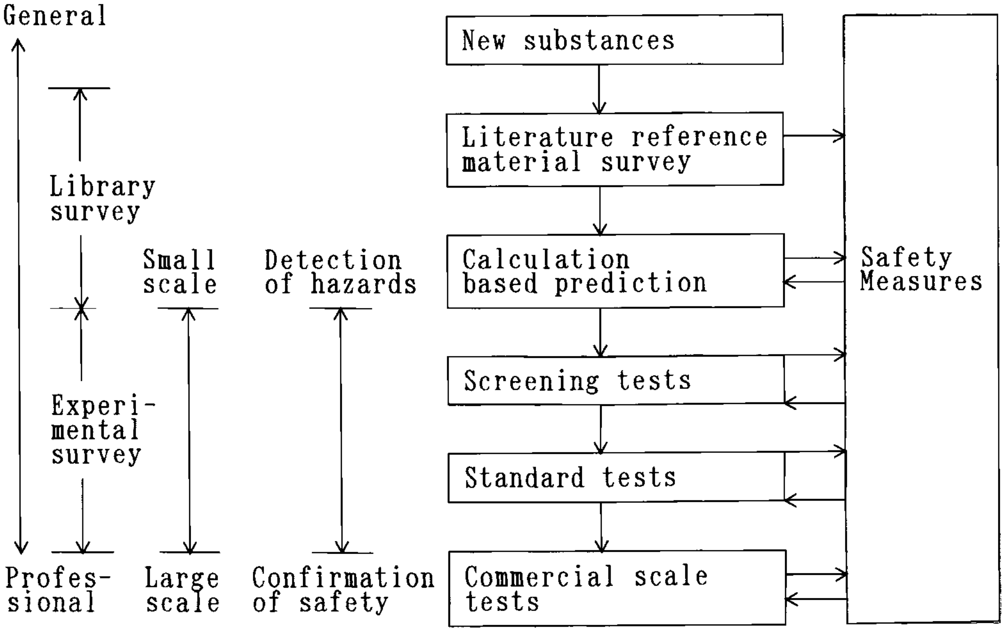

Fig. 1.1. Flow chart to evaluate hazards of reactive chemicals.

Detonation may occur if the magnitude is large. Detonation by itself generates shock waves and is very violent. Deflagration and thermal explosion, if they are violent, are a serious problem because accidental deflagration and thermal explosion may cause damage at a disasterous level. The violence of the deflagration and thermal explosion can be determined by the burning rate test or pressure increase rate test. These tests are on the border between screening tests and standard tests.

1.4.2 Procedures for the evaluation of hazards

Although progress has been made in methods of evaluating hazards for self-reactive substances, further improvement is required on the international level. To insure safety, one needs to take the measures which are consider the best for each specific occasion. The flow chart shown in Fig.1.1 has been suggested by people involved with safety to evaluate whether new substances are hazardous reactive chemicals.

If one needs to handle substances whose properties are unknown, a survey of the literature should be done first to determine whether the substances in question are known to be hazardous. If the literature provides enough information and data, no further evaluation is necessary. The substances should be treated in accordance with the instructions described in the references.
However, if reference materials indicate that the new substances may be hazardous, and if the level of their hazards is not known, then a prediction based on calculations is recommended. The advantage of a calculation is that it gives some indication of the level of hazard without requiring any experiments.
A calculation does not require any facilities like those needed for experiments, and people can easily become familiar with the calculations that enable predictions. In principle, this means that calculation can be applied more widely. However, some calculations are impossible, and occasionally the results of the calculations are not reliable. In such cases, conclusions cannot be reached on the basis of calculations alone; screening tests become necessary. Most companies and institutes which develop reactive chemicals now have appropriate facilities to run screening tests.
If a substance becomes commercialized and available in a large quantity, screening tests are not enough. Large-scale standard tests are necessary to define the safety of the substance, and if the existence of hazards is indicated by these standard tests, measures to make the safe handling of the substance possible must be sought.

1.4.3 Evaluation of hazards of fire or explosion with reactive chemicals

1.4.3.1 Survey of reference materials

The best reference for reactive chemicals may be "Handbook of Reactive Chemical Hazards" written by Bretherick (third version; 1985). Its Japanese translation has been available from Maruzen since 1987 4) . This book is the most comprehensive data source which includes examples of hazards of reactive chemicals. Descriptions of about 5,000 reactive chemicals are contained together with the list of primary and secondary references to the data. In addition, the "Group" column of the book describes specific hazards of each group of reactive chemicals having a common structure; specific terms and other topics relating to the hazards of reactive chemicals found in the "Topics" column.

In the handbook one can discover whether a substance has caused an accident in the past in reference to its specific hazards. If a particular substance is not described in this book, one can make assumptions about its probable hazards by studying other substances with similar structures.

Another survey may be made based on the presence of an explosive atomic group. This survey is helpful for substances not specifically described in Bretherick's book. A table of atomic groups characteristic of explosive substances is presented on page XXXViii of the handbook or on page 42 of Safety of Reactive Chemicals 3) . If the explosive atomic group is contained within a substance in question, the substance is probably explosive and it should be treated very carefully. Some companies that have already conducted preliminary evaluations of reactive chemicals will add the atomic group specific to unstable new substances to this table and use this information for the preliminary evaluation of additional substances.

Reactive chemicals sometimes cause an explosion after long storage. The cause of the explosion may be the generation of an explosive peroxide. In order to avoid such accidents, one should be familiar with the atomic groups which generate peroxides. These groups are listed in the table 3) 4) . Based on Bretherick's book, a table 8) of spontaneously combustible substances, water−reactive substances, and unstable substances has been prepared. This table is in the Japanese edition of this book. It may be helpful for individuals to prepare similar tables of structural formulas specific to hazardous substances by using data from references.

As items for literature surveys, the following are recommended. :

1. Examples of accidents
2. Examples symptomatic of hazards
3. Spontaneous combustibility
4. Hazardous reactivity with water
5. Generation of explosive substances (like peroxides) during storage
6. Explosiveness
7. Violence of deflagration
8. Violence of thermal decomposition
9. Instability (DSC decomposition initiation temperature)
10. High sensitivity (sensitivity to mechanical impact or friction)
11. Ease of ignition (ignitability of solid)
12. Flammability (flammability of liquid)

13. Flammability range (possibility of combustible explosion of mixtures with air)
14. Ease of generation of static electricity
15. Hypergolic ignition hazards
16. Others

All the above data may not be available from the literature. The data which are necessary but unobtainable need to be secured by calculation or experiment. For the preliminary evaluation of hazardous reactive chemicals, data sheets indicating hazards are recommended. Although no complete set of data sheets is available at present, Material Safety Data Sheets (MSDS) 9) designated by OSHA, the Department of Labor of the U.S.A. and Chemical Data Handbooks 10) issued by the Tokyo Fire Agency contain some of this data. A hazard data base which can be used for the compilation of complete data sheets should be established in the near future.

It is also useful to consider safety measures at the stage of the first literature survey. Table 1.5 indicates possible safety measures to be taken with reactive chemicals. The instructions on first aid in emergencies on Table 1.5 have been provided by the U.S. Department of Transportation 11), OSHA 9), Tokyo Fire Agency 10), and the Ministry of Health and Welfare 12).

Table 1.5 Possible Safety Measures for Reactive Chemicals

For substances	Give up the use of highly hazardous substances Make substances safe by dilution, etc.
For handling	Prohibit fire Take measures to avoid static electricity Try safe packaging
For education	Make people familiar with the hazards by MSDS, etc. to avoid errors
For facilities and processes	Adopt less dangerous facilities and processes
For emergency	Analyze possible phenomena in an emergency and make people familiar with the phenomena: Instructions on emergency first aid techniques

1.4.3.2 Prediction of hazards by calculation

If the hazards of reactive chemicals can be predicted by calculation based on their structures, as opposed to experiments, such prediction could be very useful in the overall development of reactive chemicals. There has not yet been a complete method developed, but two techniques, CHETAH 13) 3) and REITP2 14) 3), are well known in the world 3) 4).

CHETAH was developed by the E−27 Committee of ASTM : the generation heat of a single organic compound is assumed from its chemical structure by using group additivities, and explosion hazards are predicted by the results of the assumption that decomposition to products which give the maximum heat of reaction occurs.

REITP2 was developed by our laboratory at the University of Tokyo : fire and explosion hazards of single substances or mixtures are predicted by using the standard enthalpies of formation. These methods are used by some Japanese companies for the preliminary evaluation of hazardous chemicals.

Computerized programs of CHETAH and REITP2 have been prepared, but predictions by manual calculation are also possible (refer to Chapter 3[15]). Both programs require knowledge of the heat of formation of reactive chemicals. However, for some unstable substances, there are no actual measured values of generation heat of formation or data to enable the assumption of heat of formation. This is a problem for CHETAH and REITP2. These methods try to determine the possibility of explosion and burning by estimating heats of reaction. However, the probability of explosion and burning is affected not only by the heat of reaction but also by the ease with which the reaction occurs. CHETAH and REITP2 fail to take this fact into account. Table 1.6 shows the items which can be estimated by the current methods of evaluation.

Table 1.6 Hazards of Reactive Chemicals which are predictable by Calculation

Phenomenon	Types of hazards							
	Probability of occurrence		Ease of occurrence		Magnitude		Violence	
	Outline	Detail	Outline	Detail	Outline	Detail	Outline	Detail
Detonation	○				○			
Deflagration	○				○			
Thermal explosion	○				○			
Hypergolic reaction	△*				○			

* There is a possibility of hypergolic ignition but whether the ignition actually occurs is not known.

1.4.3.3 Screening tests for reactive chemicals

Screening tests are small−scale, safe experiments that provide information about hazards in a short time. It is always desirable to obtain higher quality information. We will mention only those methods which seem desirable to us based on our experience.

a. Sealed cell – differential scanning calorimetry (SC–DSC) or its equivalent method [3]

SC–DSC is so far the most useful method for screening the hazards of unstable substances. SC–DSC curves of unstable substances give valuable information on their hazards. Two of the most important points on the experimental curve are the decomposition on–set temperature on DSC TDSC (the temperature at the intersection of the base line and the extension of the maximum slope on the exothermic peak) and decomposition heat on DSC QDSC (estimated by the area of the exothermic peak).

SC–DSC enables the estimation not only of reaction heat but also the ease of occurrence of the reaction, while the calculation method provides only the estimated value of the reaction heat. Moreover, samples can be tested in the early stages of their development, because the SC–DSC requires only a small quantity of sample, typically less than 3mg per test.

A new method has recently been developed using DSC to predict whether a self reactive substance has the ability to propagate an explosion (See Chapter 3) [16]. In this method, by plotting the log of QDSC against the log of (TDSC–25), the ability of a substance to propagate an explosion can be judged by seeing on which side of a certain line the plot falls (See Fig. 1.2.).

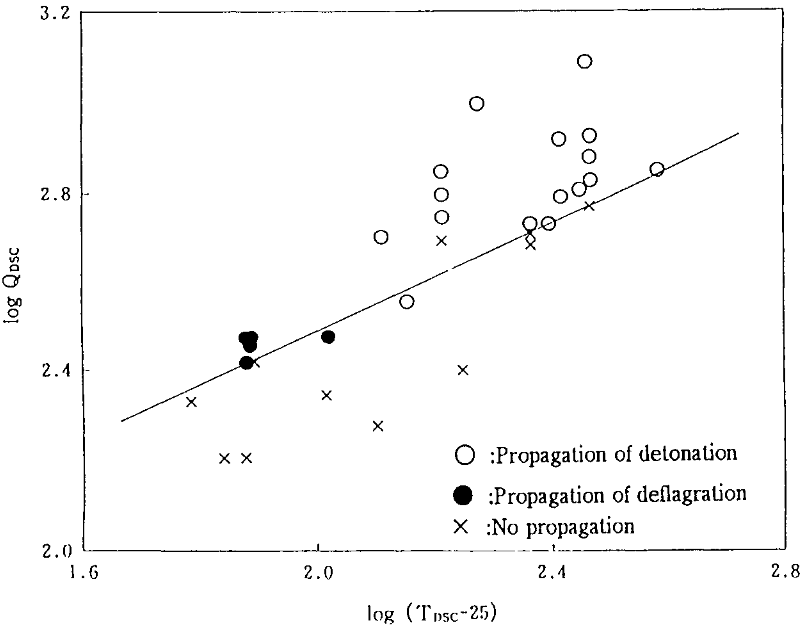

Fig. 1.2 Plots of $\log(T_{DSC}-25)$ vs. $\log Q_{DSC}$

Hazards of reactive chemicals predicted by the result of SC–DSC are shown in Table 1.7. SC–DSC has been selected for use as a test to classify hazardous materials under the Fire Services Law (See Chapter 4).

b. Drop ball test

Among hazardous reactive chemicals, special attention should be paid to those which easily explode by mechanical impact or friction. The use of these chemicals without knowledge of their characteristics inevitably leads to an accident. These chemicals include Dibenzoylperoxide (BPO), 5-chloro-1,2,3-thiadiazole (5-CT),mixtures of chlorate and red phosphorus, and 2,4-dinitro- phenylhydrazine (DNPH). Appropriate handling procedures for these highly sensitive chemicals during preliminary evaluations must be established.

5-CT, which has a history of several disasters due to explosions, poses a difficult problem because of its impact sensitivity (the ease with which mechanical impact causes explosion) [17]. This compound, having a melting point of about 20 ° C, did not explode in any of six trials when hit by a 5kg hammer dropped from a height of 1m as long as it was in the solid state. However, when melted at over 20 ° C and bubbled with air, it explodes in each of six trials when hit by merely a 100g hammer from 20cm height. Liquid explosives containing air bubbles are very sensitive.

Dry BPO is also sensitive to mechanical impact and has caused many explosions. But it is known that it does not propagate explosion when it is wet [18]. Dry 2,4-DNPH is also quite sensitive. For improved safety, reagent manufacturers are supplying 2,4-DNPH wet with water. No explosion of 2,4-DNPH has been reported, probably because it is usually distributed in small packets as an analytical reagent.

Mixtures of potassium chlorate and red phosphorus have been used as fireworks. Their sensitivity is so high that the conventional way to handle their admixture to avoid explosion is to mix the two materials wet with water, form them into a product, and then dry them. The contact mixture of silver chlorate and red phosphorus explodes merely by being hit by a 1g steel ball dropping through a few centimetres [19].

Impact sensitivity varies widely from one chemical to another. Since it is not possible to test many chemicals with wide sensitivity ranges by a conventional drop hammer test, we have begun the trial use of a drop ball tester which allows us to change the weight of falling objects over a wide range [19].

To determine the impact sensitivity of self-reactive chemicals, it is best to utilize the drop ball test using the direct hit method and indirect hit method and adopting an up and down test setting algorithm keeping the height of falling balls at constant intervals. One can obtain the 50% explosion point energy (E_{50}) and its logarithm by this method ($\log E_{50}$). The drop ball test has been selected for use as a test to classify hazardous materials under the Fire Services Law (see Chapter 3).

c. Ignitability tests

Compared to other reactive chemicals, ignitable reactive chemicals are extremely hazardous. They ignite by friction or mechanical impact, or by contacting sparks due to static electricity, or by hot surfaces or hot objects, or fire. Often their ignition leads to major disasters.

The ignitability test of the German National Material Laboratory (BAM),which is the most famous ignitability test, can now be conducted much easier than was originally prescribed, because the lighters emitting iron–cerium sparks to test highly ignitable chemicals are now readily available as acetylene gas igniters. One can use home–use igniters such as "Chakkaman" and "Gas Match", available at grocery stores, as igniters for small gas flame tests to check chemicals with moderate ignitability. If a chemical does not ignite after contacting the gas flames of an igniter designed for home use for 10 seconds, it is a relatively safe chemical which will not ignite by sparks of static electricity or heat resulting from minor friction. This test has also been adopted as a test to classify hazardous materials under the Fire Services Law (See Chapter 4). Table 1.7 shows how these three screening tests are applied.

Table 1.7 Hazards of Reactive Chemicals which are predictable by SC–DSC (QDSC and TDSC), Drop Ball Test and Ignitability Test

Phenomenon	Types of hazards							
	Probability of occurrence		Ease of occurrence		Magnitude		Violence	
	Out-line	De-tail	Out-line	De-tail	Out-line	De-tail	Out-line	De-tail
Detonation	Q_{DSC}		(I)D		Q_{DSC}		D*	
Deflagration	Q_{DSC}		I(D)		Q_{DSC}		I*	
Thermal explosion	Q_{DSC}		T_{DSC}		Q_{DSC}			
Hypergolic reaction								

* D:Drop ball, I:Ignitability

1.4.3.4 Standard tests for reactive chemicals

In this section, tests to evaluate the hazards of reactive chemicals more accurately will be introduced. They are assumed to be the best tests available to date, even though they all may not be completely perfected yet.

a. Pressure Vessel Test 3) (See Chapter 3)

The pressure vessel test is used to examine the violence of thermal explosions. The test indicates whether a runaway reaction occurs when reactive chemicals in the vessel are heated by a fire or exposure to high temperature, or if the temperature of chemicals in the reactor rises abnormally. This test needs attention because the expulsion of chemicals from inside the vessel may mix with air and cause a mist explosion.

The pressure vessel test is expected to be adopted as a standard test to check self-reactive chemicals, including organic peroxides, or unstable substances, because this method is presumed to be highly capable at detecting hazards. Under standard test conditions, the test method is : put 5g (U.S. method, Japanese method), or 10g (Dutch method), of chemicals in a pressure vessel having a capacity of about 200ml with a rupture disc with a sustaining pressure of 6kgf/cm ^{2} . Heat the vessel by a gas flame or electric heater. Measure the violence of the thermal explosion as the limiting orifice diameter at which the rupture disc tears or splits open.

This test is not very accurate, although it is widely used to evaluate the hazards of organic peroxides. A new test procedure has been developed to classify the violence of decomposition of self-reactive chemicals into three levels. In the new test, only 1mm and 9mm orifices are used. Ten trials are conducted for each diameter, and the chemicals which explode 5 times or more are classified as medium and highly hazardous materials, respectively.This test has been adopted to classify hazardous materials under the Fire Services Law (See Chapter 3).

We have sought a standard material. With 1mm orifices, a mixture of 80% AIBN and 20% inert alumina exploded 9 times while a 70% AIBN mixture never exploded. On the other hand, with 9mm orifices, a mixture of 80% BPO and 20% inert alumina exploded 10 times while a 70% BPO mixture never exploded. The boundary substance seems to fall somewhere between these mixtures.

b. Shock sensitivity test using ballistic mortar (See Chapter 3)

The ease of occurrence of explosion for a self-reactive chemical may be judged by its shock sensitivity and its ability to propagate the explosion. The shock sensitivity of highly sensitive chemicals can be measured by the drop ball test described above. However, those chemicals whose hazard can be measured by the drop ball test are too sensitive for daily use. Different methods are needed for those chemicals which are not likely to explode in daily use to determine whether a substance can cause explosion under extraordinary conditions.

A shock sensitivity test using a MkIII ballistic mortar (Variable initiator test) has been developed for that purpose [20] . One can measure the ease of occurrence of explosions for chemicals with low sensitivity which fall on the boundary of explosives and nonexplosives. The method is : place 5g of the test chemical into a 100kg mortar and initiate it with a detonator, which is equivalent to 0.2 – 2.0g of the high explosive PETN.

Adjust the amount of the initiator to find the exact amount of it as a PETN equivalent that would thoroughly initiate the 5 g of the chemical.

The determination of amount is used as the measure of sensitivity.

c. Test of ability to propagate explosion

Given a sufficiently strong initiation, chemicals with low sensitivity explode to a certain extent but, in some cases, cease exploding at a certain point. The discontinuation of explosion shows that the material is unable to propagate an explosion and therefore that the chemical cannot continue explosion by itself.

Some chemicals thoroughly explode in the sensitivity test described in subparagraph b but do not have the ability to propagate an explosion. One example of this is a composite rocket propellant consisting of ammonium perchlorate, polybutadiene, and aluminum powder. The propellant (15g) thoroughly explodes by one No.6 detonator (PETN equivalent is 0.6g) in the ballistic mortar test. However, it does not show the ability to propagate an explosion when a solid block of the propellant is put in a steel tube with inner and outer diameters at 50mm and 60mm, respectively, and is initiated by 50g of a high explopsive booster (BAM 50/60 Steel Tube Test) (See Chapter 5 Ref. 21).

Although the BAM 50/60 steel tube test [3] has been considered the best method to prove the lack of ability to propagate an explosion, one drawback was pointed out recently. Namely, it is difficult to judge the ability to propagate an explosion for those explosive substances such as BPO with small explosive power, because the steel tube does not break into pieces even if the explosion is propagated. This problem can be overcome by doing this test in sand and measuring the capacity of the crater created [22], or by doing this test in water to measure the actual explosion energy [21].

In order to predict the ability to propagate an explosion by DSC as described, standard chemicals are needed which fall on the boundary of having ability to propagate explosion or not. The boundary determining chemicals include a mixture of 80% BPO and 20% water and a mixture of 70% 2,4−DNT and 30% inert alumina.

d. Deflagration violence test

Many tests have been proposed to examine deflagration violence [23]. Much attention has been given to an improved time/pressure test to measure ignitability and violence of deflagration.

Though a mixture of oxidants and flammable substances are self−reactive substances, they are regulated as oxidants in Japan. The following classification test method applies in this case: Pile up 30g each of two mixtures of sample and wood meal into a cone−shape in the ratio of 1:1 and 8:2 in mass, respectively. Ignite each with wire heated at 1,000 ° C that surrounds the bottom of the pile. Determine the burning velocity by measuring the time from ignition to the extinguishing of the flame. Potassium bromate and potassium perchlorate are used as standard oxidizing agents.

e. Test of self−accelerating decomposition temperature (SADT) [3]

When exposed to high temperature for a long time, a self−reactive substance may cause a thermal explosion by reacting gradually with itself and accumulating reaction heat. The temperature which causes self−accelerating decomposition is called internally SADT. In the hazardous substance transportation business, SADT is defined as the temperature which causes self−accelerating decomposition within a week in the package used for transport.

There are several SADT test methods. BAM's accumulated heat storage test [3] is considered to be superior in practicality and credibility. :

Put 400ml of sample into a 500ml dewer vessel. Put on the lid of the heat insulator. Put the vessel in a constant temperature chamber. Measure the temperature to indicate the start of self–heating and the self–accelerating decomposition. The method is very useful but it cannot apply to a substance which has a high vapor pressure, such as 5–CT. Chemical and pharmaceutical companies in Europe use a method to measure heat stability of solid deposit [3]. The method applies to the drying process of powder products to avoid accidents. It is not yet used in Japan.

The details on the methods described above are found in Chapter 4 of "Safety of Reactive Chemicals" [3] and Chapter 3 of this book.

Table 1.8 shows the applicable ranges for these standard test methods.

Table 1.8 Hazards of Reactive Chemicals evaluated by the Pressure Vessel Test (PV), MkIII Ballistic Mortar Test (MkIII), BAM 50/60 Steel Tube Test (50/60), Test of Deflagration Violence (DF), and SADT Test (SADT)

Phenomenon	Types of hazards							
	Probability of occurrence		Ease of occurrence		Magnitude		Violence	
	Out-line	De-tail	Out-line	De-tail	Out-line	De-tail	Out-line	De-tail
Detonation		50/60		MkIII	MkIII	50/60 (SW)*	50/60	50/60 (SW)*
Deflagration		50/60 (SW)*		MkIII DF		MkIII 50/60 (SW)*		MkIII DF
Thermal explosion	PV		PV	SADT				PV
Hypergolic reaction								

* (SW) means that the 50/60 Steel Tube Test is conducted under sand or water.

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Chapter 2

ACCIDENTS INVOLVING REACTIVE CHEMICALS

2.1 Introduction

Past accidents, as realistic evidence for the possibility of accidents to come, are very instructive. Learning about past accidents should prevent the occurrence of similar accidents. However, in view of the many cases in which the same accidents have occurred repeatedly, learning about previous accidents is all the more necessary.

In this chapter, reactive substances will be classified into several types; for each type, major informative past accidents will be described. Accidents involving hazardous materials in earthquakes will also be discussed here.

2.2 Accidents Involving Self–Reactive Substances

Self–reactive substances, having been used in large quantities and having caused accidents, are frequently regulated. Categories of self–reactive substances include: explosive substances (low explosives) designated as Class 1 by the U. N., self–reactive substances designated as Class 4.1, organic peroxides designated as Class 5.2, and ammonium nitrate and ammonium perchlorate among oxidsizing substances designated Class 5.1.

The OECD–IGUS (Organization for Economic Cooperation and Development – International Group of Experts on the Explosion Risks of Unstable Substances) has 4 working groups, three of which are related to self–reactive substances :

1. Kertichjers and Commecial Explosives;
2. Energetic and Qxidising Substances;
3. Sensitivety and Propagation.

(2 and 3 are now 1 group.)

These were supposedly chosen as subjects of research because of their use in large quantities and because of the history of accidents involving them. In the following sections, accidents with self–reactive substances, including those listed above, will be described.

2.2.1 Accidents with nitrocellulose and substances containing it

Nitrocellulose was invented in 1845 by Schonbein, a professor at the University of Basel. It quickly drew attention from the academic circle: first, as a material for a fiber with silky feel, but ultimately as a raw material for the production of celluloid, lacquer, smokeless powder and dynamite.

2.2.1.1 Nitrocellulose

On July 14, 1847, two years after the invention of nitrocellulose,an accidental fire caused by the spontaneous ignition of nitrocellulose occurred in a factory producing it in Great Britain. Twenty lives were reportedly lost 1) . In 1948, a fire took place in a nitrocellulose warehouse in France. For a period of sixteen years after this accident, production of nitrocellulose was prohibited in Great Britain and France. In the U.S.A. and the U.S.S.R. it was also temporarily prohibited.

In Japan, an accident involving both fire and explosion at the Katsushima Warehouse on July 14, 1964, is a famous incident. The fire was initiated by the ignition of canned nitrocellulose in an open–air storage facility and, during the fire fighting, methyl ethyl ketone peroxide in storage exploded to kill 19 people and injure 158 4) . In the Faculty of Engineering, Yamagata University in 1984, nitrocellulose that had been stored for many years ignited spontaneously.

Nitrocellulose is dangerous because of its properties: liability to spontaneous ignition; and, when dry, liability to ignition by spark, impact, or friction, to electrostatic charging, and to heat accumulation leading to ignition followed by very quick burning. Because of these properties, many accidents have been caused by spontaneous ignition or by ignition due to impact or friction during production, drying, or storage. To prevent such accidents, an improved purification method to produce stable nitrocellulose (Abel, Great Britain, 1869) and methods of handling nitrocellulose wet with water or alcohol have been developed; wetting with about 20% of water or alcohol reduces the flammability of nitrocellulose and makes its burning much milder.

2.2.1.2 Celluloid

Celluloid, an artificial plastic made from nitrocellulose and camphor, was invented by Parkes from Britain and the Hiatt brothers, printers in the U.S.A. (USP 88634 (1869)).

The inventions of photographic films by Eastman Co. in 1885 and of movies by Edison in 1895 markedly expanded the demands for celluloid, bringing about a major increase in large scale accidents, the effects of which were magnified by involving many people in enclosed spaces.

According to a survey by Kogaku Komamiya 2) , a film fire during the showing of a movie in the U.S.S.R. in 1929 killed 144 people. In Japan there were 40 fires that happened during the showing of movies in 1930, and 70 in 1951, for which the loss of 124 lives was recorded.

A fire of celluloid film that became a news item in Japan in recent years occurred in the National Modern Museum [3]. The fire, at about 14:47 on September 3, 1984, was caused by the spontaneous ignition of nitrocellulose films in the film storeroom on the fifth floor of the museum. The fire damaged a considerable number of the 3,000 reels of foreign movies that were stored there. On December 16, 1932, a disastrous fire caused by the burning of celluloid toys on a counter of Shirakiya Department Store resulted in the death of 14 saleswomen who could not escape and the injury of 21 other people.

The dangerous properties of celluloid originate from its principal component, nitrocellulose. Four of the most important are: spontaneous ignition, liability to ignite on heating, liability burn vigorously with the generation of toxic gas, and reactivity with nitrogen, making nitrogen fire extinguishing methods inapplicable. The effort to prevent accidents with celluloid has chiefly concentrated on laws and regulations, as exemplified by its regulation as a Class 5 Hazardous Goods in the Fire Services Law, the enforcement of the Rule for Control of Celluloid Plants (1937), and the enactment of the Movie Film Operator QualificationSystem.

On the other hand, research in the U.S.A. to develop nonflammable film was carried out in the 1930s. In Japan, the ratio of nonflammable photographic films to flammable ones reached about 80% in 1955; all photographic films have been made of cellulose acetate since 1958. Celluloid films are still being produced in very limited quantities, and the present celluloid production in Japan is about 500t/year. Fires caused by the spontaneous ignition of celluloid within the jurisdiction of the Tokyo Fire Services Agency numbered a record high of 39 cases in 1953 but have decreased year by year since that time.

However, they still continue to take place at an average rate of three cases per year [3].

Eastman Kodak Co. and Fuji Photo Film Co., Ltd., both major producers of photographic film, are earnestly committed to providing safe films.

2.2.1.3 Smokeless powder

Smokeless powder has properties similar to nitrocellulose and celluloid and has produced many accidents by spontaneous ignition, although many have not been disclosed because of requirements of military secrecy. Many explosions of magazines in warships in particular have occurred because of the spontaneous ignition of smokeless powder. However, in the famous novel "Mutsu Sank by Explosion" written by Akira Yoshimura, a documentary novelist, most warship explosions were mentioned as having been fictitious accidents.

Studies on the stability of smokeless powder are currently being continued, the results of which are presented at the "Conference on Chemical Problems Related to Safety of Explosives" held every three years in Sweden.

2.2.2 Accidents involving ammonium nitrate

Ammonium nitrate, both an oxidizer and a self-reactive substance, is still used in fertilizers and as a raw material for explosives. The following two are typical accidents involving ammonium nitrate.

2.2.2.1 Explosion of ammonium-sulfate nitrate double salt fertilizer at Oppau

A disastrous accident occurred at a BASF's plant in Oppau, Germany, with two explosions at 7:29 and 7:31 a.m. on September 21, 1921, resulting in a casualty list of 509 dead, 160 missing, and 1,952 injured.

The plant and about 70% of the 1,000 nearby houses were destroyed by the explosions.

In Heidelberg, about 22km from Oppau, earthquakes from the two explosions were felt first, and 82 seconds later the blast broke windows and doors and damaged gas tanks, oil tanks, and cargo boats on the river. The blast produced damage in Frankfurt 85km away from the site of the explosion, and the roaring sound and earthquake reached as far as Bayreuth, 230km distant.

The cause of the accident was the blasting with dynamite of about 4,500t of a solidified mass of ammonium sulfate nitrate compound fertilizer (a double salt of ammonium sulfate and nitrate in a mole ratio of 1:2). This process had been practiced under supervision for many years, and about 30,000 blasting procedures had been experienced without accidents until the Oppau disaster.

Experiments conducted later indicated great difficulties in making this double salt explode [5]. The above case presents an example of a substance, judged non-explosive by an ordinary explosion test, which can explode after a large scale initiation involving a very large quantity of material. Furthermore, this provides an example which suggests that very careful consideration in the evaluation of hazardous goods is essential.

2.2.2.2 Fire and explosion of an ammonium nitrate transport ship in Texas City [37]

At about 8:10 a.m. on April 1, 1947, in the port Texas City in the U.S.A., an outbreak of fire on bagged ammonium nitrate fertilizer loaded on the French cargo boat, Grand Camp, was discovered. A large quantity of ammonium nitrate fertilizer, 2,280t, was aboard. An effort was made to extinguish the fire with water spray, but the insufficient volume of water at the beginning actually increased the force of the fire, which had become uncontrollable by the time a sufficient water spray became available. The sailors were ordered to escape, but a large explosion occurredat 9:15 a.m. killing all people present, including firemen on the dock and many onlookers. The fire leaped to other places in the port, ignited oil tanks, and continued to burn for about a week.

The American cargo boat, High Flier, loaded with 960t of ammonium nitrate fertilizer and 2,000t of sulfur was in the harbor. Its sulfur cargo began to smoke at about 6:00 p.m. and initiated a large explosion at 1:00 a.m. on April 17. This sank the boat and resulted in a great disaster, the death of 552 people and injury to 3,000 of the total population of 15,000.

Evidence exists that ammonium nitrate had been handled without the knowledge that it could give rise to such terrible results. It will not ignite when one tries to ignite a small batch; even a detonator cannot initiate its explosion under normal cirumstances. However, when ammonium nitrate is present in a large quantity and comes into contact with fire involving flammable goods in a confined space, it can produce a major explosion of the type seen in Texas City.

2.2.3 Accidents of organic peroxides

Organic peroxides belong to a group of relatively new self-reactive substances, which, having a broad application as polymerization initiators, have grown with advances in petrochemistry.

Explosions of many dangerous organic peroxides, such as methyl ethyl ketone peroxide and dibenzoylperoxide, frequently occurred in the early years of their use. In developed countries, however, products made safe through dilution or other means have come on the market because of progress in research. In new developing countries on the other hand, accidents with organic peroxide in plants or during transportation still occur.

2.2.4 Accidents of other self-reactive chemicals

Accidents of classical self-reactive substances have been described in previous sections, and those of newer ones are introduced below.

2.2.4.1 DPT (Dinitrosopentamethylenetetramine)

At about 6:15 a.m. on July 28, 1979, at the 4th pier of the Maya Wharf of the Kobe Harbour, one of a group of containers stacked in the open-air emitted a fire accompanied by the roaring sound of an explosion. About 250 of the 50kg-drums in the exploded container were blown into the surrounding area. Because it was early morning and no people were nearby, no injuries or deaths were recorded. The cause of explosion was thought to be the spontaneous ignition of DPT, a rubber foaming agent. Although the case did not become a social issue because no casualties resulted, the Ministry of Transport organized the Committee for Evaluation of Properties of Hazardous Goods to carry out evaluation and classification of dangerous properties of marine-transported chemicals.

DPT had actually caused a number of fires before this case and had been designated a semi–hazardous substance in Fire Services Law. This case is another example of an accident happening when a hazardous material is not handled in an appropriate way.

2.2.4.2 5–CT (5–Chloro–1,2,3–thiadiazole)

At about 6:05 p.m. on May 14, 1980, at a chemical plant in Saitama Prefecture, an explosion making a huge roaring sound occurred which killed two persons, injured 13, and damaged the glass plates in the windows of 390 houses in the surrounding area.

The explosion was caused during the handling of the chemical 5–CT. This substance had given rise to an explosion in a West German chemical plant in January, 1978, with casualties of 3 dead and 4 wounded; immediately after this accident, the Materials Testing Laboratory of the Federal Republic of Germany evaluated the explosion hazard and other properties of this substance and concluded that it was a highly dangerous material 6) . Regrettably, Japan was not informed of this case.

At the authors' laboratory, the hazards of 5–CT leading to explosions and fires were investigated in detail 7) . It was found that 5–CT readily ignites in a container with percussion or friction, readily explodes once ignited, and drastically explodes upon being heated by the surroundings, having an explosive power of about 80% of the high performance explosive TNT.

Accordingly, it was deemed a substance too dangerous to be produced in an ordinary chemical plant. On the other hand, it was also found that its dangerous properties were not easily identified by some commonly practiced test methods; an ordinary differential thermal analysis did not give a result suggestive of the danger, and a drop weight sensitivity test of solid 5–CT indicated that the substance was insensitive to percussion.

The structural formula of this substance indicates the presence of a functional group characteristic of an explosive substance. This structure cannot be the decisive factor because other substances having the same functional group are not necessarily as dangerous as 5–CT. It is now clear that correct evaluation of the dangerous properties of a substance such as 5–CT cannot be achieved unless several evaluation methods are applied in parallel. At present, there are no judicial regulations for 5–CT in Japan, because it is not very common and hence is not considered dangerous.

The accident at Saitama influenced the people involved profoundly,and it become a journalistic topic within newspapers and other media. The Japan Chemical Industry Association formed the "Workshop for Unstable Substances" and issued the brochure "For the prevention of unpredictable explosion and fire caused by chemical substances" in September of the year as an immediate measure. The association, after repeating its additional studies, issued the brochure "Guidelines for the prevention of disasters from unstable substances" in September, 1982, in which suggestion were offered regarding the kinds of provisional tests that should be made before a new chemical substance is

handled.
Responding to the above action, the Japan Carlit Co., Ltd. provided a facility to conduct tests as a business for the evaluation of dangerous properties. Accidents are tragic, but one cannot deny that the explosion involving 5−CT became a lesson that has promoted measures for prevention of accidents with explosive and self−reactive materials.

2.2.4.3 Germane (GeH_4)

At about 10:20 a.m. on November 26, 1984, at a plant in Kawasaki City, a bomb containing germane was broken when it was being unloaded, and caught fire burning two workers. It was consequently recognized that some of the semiconductor raw materials that were thought not to be dangerous explosives are unbelievably dangerous, and that this type of accident produces a great economic loss.

2.3 Accidents During Chemical Reactions

There are numerous accidents that have occurred during a chemical reaction or process [8]. Three instructive examples will be described in the following sections.

2.3.1 Sulfonation

The first example is an accident (August, 1970) which occurred during the process of coproducing m−benzenedisulfonic acid and toluenesulfonic acid by the simultaneous sulfonation of benzene and toluene in the same reactor. One person was killed and 6 wounded [9].
At the final step of the reaction, when toluene at 110 ° C was charged into the reactor, the stirrer stopped. After the repair of the stirrer, stirring was resumed, but the vapor blew out and an explosion occurred. In the past, a considerable number of accidents have been known to occur during sulfonation. Although sulfonation has been thought to be of a lower exothermic potential than nitration, it has given rise to many unexpected accidents from a variety of causes: the reaction sometimes does not start smoothly; sulfonic acid at high temperature decomposes with a considerable heat generation; and the flammable mist blown off can catch fire.

2.3.2 A runaway reaction producing a diffusible toxic substance

The accident during the chemical process described below is an example of a runaway reaction producing a toxic substance which results in environmental pollution [10].
At about 0:40 p.m. on July 10, 1976, at a chemical plant in northern Italy, a safety plate of a reactor fractured, blowing the leaking substance into the sky as a white cloud. The cloud was carried on the wind toward the town of Seveso and was conveyed to the ground there by falling rain. The substance leaked contained the highly toxic material

dioxin, which was formed by the runaway reaction.

Several days after this happened, cows, pigs, and other farm animals, bleeding at the nose, died one by one. Then people, as many as 220,000, complained of exanthema, contact dermatitis, and nausea. Highly exposed people from nearby regions were moved to other places in groups, among whom many cases of stillbirth and dystocia were found later. This highly toxic substance, dioxin, is an especially difficult problem because it is not produced during a normal reaction but only during an abnormal reaction.

2.3.3 A big accident in a polymerization process as a trigger

At about 5:25 p.m. on August 21, 1982, at a chemical plant in Sakai City, Osaka, an explosion led to a major accident with casualties of 4 dead, 8 seriously injured, about 200 lightly injured, and damage to about 2,000 nearby houses [51]. The site of the accident was a plant producing a copolymer of acrylonitrile and styrene. On the preceding day, August 20, at about 0:25 a.m., a small explosion had taken place at the deodorizing apparatus attached to the main reactor, which induced fractures at more than a dozen locations on the ducts connecting reactors to the deodorizer.

The big explosion on August 21 was thought to have been induced by the small explosion on the preceding day. This accident provides a lesson that a small accident can initiate a larger one.

2.4 Accidents Involving Reactions With Other Substances

2.4.1 Accidents caused by contact with air

2.4.1.1 Silane (SiH_4)

At about 8:30 a.m. on October 3, 1982, a fire occurred at a VLSI manufacturing plant at Kiyotake-cho, Miyazaki Prefecture, burning the ceiling of a partly two-story ferro-concrete building. Two employees were seriously injured, two lightly injured, and one fireman was overcome by toxic gas. The fire, not large in scale, drew much attention from experts because it was in a plant at the cutting edge of high technology and the ensuing economic loss was great. The cause was thought to have been the spontaneous ignition of silane (SiH_4) leaking into the air.

As the result of this fire, the production of 3 million integrated circuits per month, reportedly corresponding to sales of more than ten billion yen, stopped for several months, and the damage to the facilities exceeded 2 million yen per square meter of area. Spurred by this accident, classes on the safety of semiconductor gases are now held frequently, and guidelines for the safe handling of semiconductor gases have been established.

2.4.1.2 Formation of peroxides

Many cases are known in which the storage of a substance for a long period of time in contact with air causes explosive peroxides to form and accumulate. These peroxides may eventually explode and cause an accident [11] .

2.4.2 Accidents caused by contact with water

2.4.2.1 The tragedy of Bhopal [12]

The accident involving the generation of heat and the leakage of methyl isocyanate (MIC) that happened in Bhopal, India, from midnight of December 2 through Dec. 3, 1984, developed into the greatest industrial disaster in history. The death toll was reportedly 2,500, and it was said that more than 10,000 people suffered health–disorders as after–effects. Approximately 200,000 people in total were affected by the leaked gas.

The chemical, MIC, that leaked and thereby caused this great disaster, is a highly toxic substance said to have a 50% lethal concentration (LC_{50} , or that concentration killing 50% of a population of experimental rats after a 4–hour exposure) of 5ppm. This degree of toxicity may be brought into perspective by comparing it to the toxicity of phosgene, noted as a poison gas, the LC_{50} of which is 50ppm for rats.

MIC is a highly volatile liquid with a boiling point of 39.1 °C. MIC vapour is heavy, with a specific density 1.97 times that of air, and flows downwind in the air moving along the surface of the ground. Because the accident occurred at midnight when the atmosphere was stabilized, as the MIC leaked it did not diffuse upward but rather covered the ground and moved downwind. MIC vapour is a powerful irritant, and the injured people are thought to have felt much pain. With no information available in the midnight hour, people did not even know in which direction they should try to escape.

It was known that MIC reacts with water to liberate carbon dioxide with the accompanying generation of heat, which causes the pressure in a closed container to increase. MIC can be detoxified by treatment with aqueous caustic soda or by combustion in the air. The storage facility for MIC in Bhopal had safety equipment installed to enable the detoxification of MIC, but the equipment did not work at the time of the accident.

By the analysis of the solid substance remaining after the accident in the leaking storage tank, it was found that half of the substance was a product of a trimolecular reaction of MIC. The formation of this and other products was thought to have been caused by the following sequence of events: considerable amounts of water and chloroform were mixed with MIC causing an increase in temperature and hence the melting of the tank wall, which then continued to catalyze the abnormal reaction.

Just after 10:00 p.m. on December 2, 1984, the inside of the piping near the MIC reactor was washed. It is speculated that a metal sheet that prevents the mixing of water with MIC was not inserted into the line at that time. At 11:00 p.m. a report was made that the pressure of the No.610 tank, that later began to leak, was 10psig, although it was 2psig at the preceding reading. This was not viewed as abnormal because the tank was frequently operated in the pressure range of 2–5psig.

At 11:30 p.m. MIC was found to be leaking, but the location of the leak could not be identified. The pressure of the tank rose sharply at 0:15 a.m. on December 3. A rattling noise was heard in the direction of No.610 tank, a noise was also generated at the safety valve, and heat was felt on the skin of the tank.

The supervisor turned on the switch for the exhaust gas scrubber in order to detoxify the MIC, but the scrubber had been closed for a maintenance inspection. The flare stack to detoxify the exhaust gas by combustion had also been removed for a maintenance inspection and was of no use. About 23t of MIC vapor tore out the fracture plate, broke the safety valve, and flew out of the exhaust–gas scrubber to a height of 33m for two hours without being detoxified by the scrubber or the flare stack. After erupting, the vapor crept downwind over the residents, supposedly because of the stabilized atmospheric conditions and because the vapor was heavier than air.

There have been numerous discussions about this accident, which produced the most casualties in the history of industrial disasters. Some arguments revolve around the direct cause of the accident. As is generally known, many major accidents have been caused by combinations of small accidents. The accident in Bhopal also happened as the result of a combination of serious mistakes: the mixing of water with MIC caused by neglecting to put the metal sheet in place to separate reactive components, and the failures in operation of the exhaust gas scrubber and the flare stack. Such cases are frequently found where a safety device is temporarily removed because the device is troublesome. It is necessary to educate people that the reliability of a safety device should be tested and that the failure of a safety device can lead to unexpectedly terrible results.

This accident has also been discussed in terms of a comparison between developed countries and developing ones. The developing countries are considered likely to fall prey to major accidents because of technological imbalances within them and because of less interest in safety. There is some truth in these statements.Even in Japan, many accidents have involved subcontractors. Hazardous goods need to be handled only in places where their dangerous properties are well understood and appropriate safety measures can be taken.

MIC has been regulated as a flammable liquid rather than a toxic substance. Its transportation has been permitted as a low–flash–point liquid of Class 3.1, by International Maritime Dangerous Goods Code (IMDG Code) or Japan's Dangerous Goods Ship Transportation and Storage Code. Considering the experience with the above accident, the rules for its handling should perhaps be altered.

An accident comparable to that of Bhopal was the runaway chemical reaction mentioned previously that liberated toxic dioxin (LD_{50} for Guinea pig = 0.6 μ g/kg) and which occurred in Seveso, Italy, on July 10, 1976. Both accidents turned out to be major disasters brought about by the liberation of a toxic substance, but, in view of the differences in the specific causes, a comparison on the same level might not be possible. As the accident in Seveso showed that the diffusion of toxic substance can lead to disaster,the people of Bhopal in the latter case who were in charge of the handling a toxic substance should have been able to avert disaster by putting that lesson to practical use.

2.4.3 Accidents caused by the mixing of mutually reactive substances

In Japan, accidents caused by the mixing of incompatible or mutually reactive substances have been experienced in earthquakes. They will be described in the following section.

2.5 Accidents Involving Hazardous Goods in Earthquakes

2.5.1 Hazardous goods causing fires in past earthquakes

2.5.1.1 Causes of fire in earthquakes in Japan

Table 2.1 lists the Great Kanto Earthquake and other major earthquakes in Japan, with the numbers of fires and a breakdown of causes for each.

Table 2.1 Causes of fires in major Japanese earthquakes

Name of earth-quake	Great Kanto[1] 11:58 a.m. September 1, 1923		Fukui[3] 4:13 p.m. June 28, 1948		Niigata[6] 1:01 p.m. June 16, 1964	
Cause	Chemicals	44	Kamado oven	8	Crude oil	4
	Kamado oven	33	Chemicals	5	Chemicals	2
	Cooking range	15	Factory furnace	4	Propane bomb	1
	Gas	9	Home oven	3	Oil pan	1
	Oil pan	5	Shichirin oven	2	Bath	1
	Electric leakage	1	Spreaded fire	2		
	Building		Bath	1		
	destruction etc.	56	Match	1		
			Unknown	3		
Total Number of fires		163 (Tokyo-fu)		29 (Fukui City)		9 (Niigata City)

Table 2.1 (Continued.)

Name of earth-quake	Tokachi Offshore[9] 9:49 a.m. May 16, 1968		Miyagi Offshore[11] 5:14 p.m. June 12, 1978	
Cause	Oil stove	20	Chemicals	3
	Coal stove	3	Electric	2
	Oil cooking range	8	Oil leakage	2
	Chemicals	4	Refiring	1
	Electric	3	Match	1
	Propane gas	2	Fall of Flammable Goods	1
	Rentan range	1	Gas tank	1
	Heavy oil burner	1	Chimney	1
	Unknown	3		
Total Number of fires		45		12

Table 2.1 (Continued.)

Name of earth-quake	Urakawa Offshore[12] at 11:32 a.m. March 21, 1982		Middle Japan Sea[14] at 0:00 p.m. May 26, 1983	
Cause	Gas rice-cooker	1	Crude oil	1
	Electric	1	Electronic lighter	1
			Match	1
			Unknown	1
Total Number of fires		2		4

The data shown in the table are different depending on references[15-29]. The percentage of fires caused by different things in each earthquake is indicated in Fig.2.1. The data shown here do not include fires (such as the ones in Yokohama and Yokosuka) for which references were not available. As to fires in foreign countries, only those with references available will be described in corresponding sections.

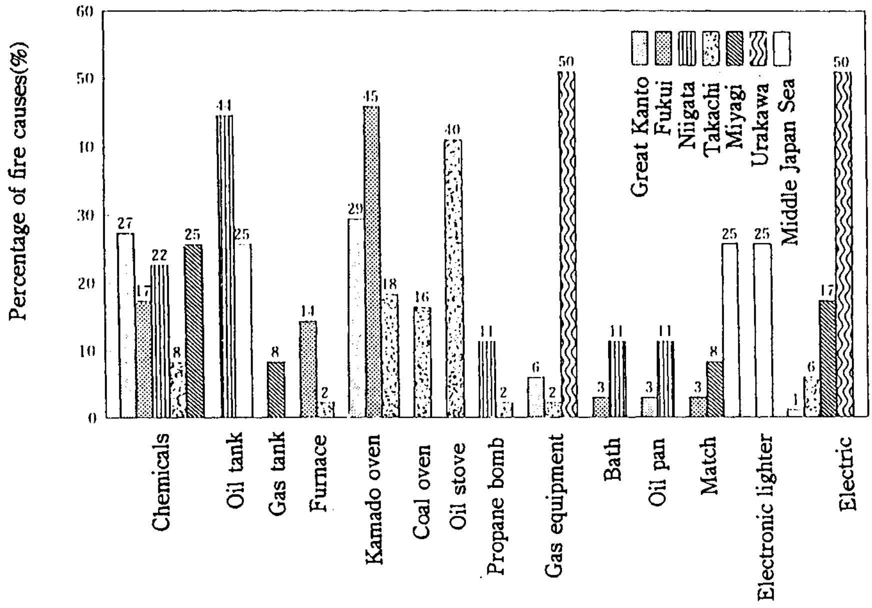

Fig 2.1 Cause comparison of fires in Japanese earthquakes

2.5.1.2 Chemicals

Chemicals placed in schools, laboratories, and pharmacies were the hazardous goods causing the largest numbers of fires in the past earthquakes. Table 2.2 lists chemicals recorded as having caused fires. Chemicals with high frequencies of causing fires in earthquakes are: volatile substances (17 cases), reactive substances mixed as a result of earthquakes and reactive chemicals contacting oxidizing agents (14 cases), yellow phosphorus igniting spontaneously (over 13 cases), alkali metals reacting with water (over 11 cases), and acids or alkalis causing fires (10 cases). It is understandable that those listed here are chemicals that require special attention in case of earthquakes.

As to places where fires caused by chemicals occur, schools —— universities, colleges, high schools, junior high schools, and elementary schools —— are the largest in number (27); incidences involving laboratories (23), production and sales sites (19), and hospitals and pharmacies (4) are highly frequent. These places all have greater likelihood of having fires caused by chemicals in earthquakes.

Recorded cases of fires will be described below for each type of place.

a. Schools

The Great Kanto Earthquake

Surveys of chemical fires in the Great Kanto Earthquake by Shuichiro Ochi [16], Professor Seiji Nakamura [15], and Kazuyuki Inoue [30] are well known. The specific chemicals involved are described in detail in reference [16], the places where fires occurred in reference 15), and the spread of the resultant fires in the reference 30).

Table 2.2 Number of chemical fires in the past earthquakes

Name of chemicals	Earthquake				Type of fire
	(1)	(2)	(3)	(4)	
White phosphorus	12		1		A
Sodium	7	2	1		B
Lithium		1			B
White phosphorus or sodium	3				A or B
Potassium permanganate and organic substances			1		B
Sodium peroxide and organic substances	1				B
Chromium trioxide and organic substances		1			B
Quick lime and water	1				B
Volatile substances	14	2	1		C
Hydrogen	1				C
Celluloid	1				C
Oxidizing agent, strong acid and volatile substances	10				B
Oxidizing agent, strong acid and organic substances	1				B
Conc. nitric acid and wood	2				B
Strong acid, alkali and volatile substances	4				B
Strong acid, alkali and fatty oil	1				B
Strong acid, alkali and floor board	1				B
Strong acid and volatile substances	1				B
Fuming sulfuric acid and floor board	1				B
Unknown (chemicals)	6	2	1	3	D

Name of earthquake :

(1) Great Kanto Earthquake (2) Miyagi Offshore Earthquake
(3) Niigata Earthquake (4) Tokachi Offshore Earthquake

Type of fire :

(A) Spontaneous ignition (B) Mixing–in and contact
(C) Catching fire (D) Most possibly by mixing–in and contact

The survey by Professor Nakamura was carried out with the cooperation of 36 students who were then enrolled in the Faculty of Physics, Tokyo Imperial University. Among the students were found the names of Kiyo–o Wadachi (now Chairman of the Central Pollution Commission, and Chairman of Fire Prevention Commission) and Kaneichi Nakata (former Chairman of Fire Prevention Commission), both actively working at the forefront of earthquake disaster prevention even today 15).

According to the survey by Professor Nakamura, 163 fires in total occurred in Tokyo

City and its suburban areas, one fourth of which, or 44, were fires caused by chemicals, among which about three fourths, or 31, were immediately extinguished. Table 2.3 shows schools on record that had chemical fires in the Great Kanto Earthquake.

Table 2.3 Schools that had Chemical fires in the Great Kanto Earthquake

Destruction by fire
Tokyo Imperial University (Medical Chemistry, Applied Chemistry, and Drug Chemistry, Faculty of Agriculture)
Waseda University, Faculty of Science and Technology (Chemical storehouse of Applied Chemistry)
Keio Medical University
Tokyo Technical College (Applied Chemistry)
Yokohama Technical College (Applied Chemistry)
Military Academy Preparatory Course (Science lecture room)
Japan Dental and Medical College
Meiji Pharmacy College
Gakushuin University (Chemicals room)
Elementary school at Manadzuru
Small fire (immediately extinguished)
Tokyo Imperial University, Fuculty of Medical Science (four pharmacy lecture rooms, drug lecture room, out–patient room)
Jikeiin Medical University
Tokyo Technical College (two locations)
Women's College (Takada–toyokawa–cho, Koishikawa–ku)
Senshu Girls' Senior High School
Kojimachi Higher Elementary School
Other schools in the suburban areas (records not available)

(i) When a fire occurred in the medicinal chemistry lecture room of the Faculty of Medical Science, Tokyo Imperial University, firemen of the Hongo–Komagome Branch Office started toward that facility under orders of the Forth Hongo Fire Services Office. On their way there, they noticed a fire in the applied chemistry lecture room of the Faculty of Engineering and worked to extinguish it, having assumed it to be the fire they were ordered to combat. Thus, the fire in the applied chemistry lecture room was soon extinguished, but the library and other facilities of the Faculty of Medical Science were consumed by fire.

(ii) Many chemical fires were extinguished by dousing them with sand, as can be seen in the examples of the Commerce and Industry Promotion Office of the Tokyo Prefectural Government, the drug lecture room of the Faculty of Medical Science, Tokyo Imperial University, and the Institute of Hygienic Sciences, the Ministry of Home Affairs.

The Fukui Earthquake

The records of damages in the Fukui Earthquake can be found in references 18, 19, 29).

Many school buildings were completely destroyed due to a large number of chemical fires; this is recorded in reference 20). Six elementary schools were burned down, five middle schools, and one high school 18). In Fukui City, two elementary schools, two middle schools, and one high school were destroyed by fire; one of them was a chemical fire 19).

(i) According to the Fire Services Head Office of Fukui City 19), a movie was playing at a PTA meeting of the Haruyama Elementary School. The building was a wooden one-story structure which collapsed and burned, killing 100 persons. The fire was thought to have been started by chemicals in the science room adjoining the room where the movie was being shown. In other references 18, 19), there were no records indicating this many victims.

(ii) Reference 29) describes a talk given by a teacher from the Haruyama Elementary School about his experience at the scene.

(iii) A chemical fire occurred in the laboratory of Fukui Technical College, but it was extinguished immediately 19).

The Niigata Earthquake

(i) In the science room of the Higashi-Niigata Middle School, Niigata City, the vibration of the earthquake on June 16, 1964 at about 1:02 p.m. caused a shelf containing chemicals to tip over, and containers of yellow phosphorus, red phosphorus, metallic sodium, magnesium, concentrated sulfuric acid, gasoline, and others chemicals fell to the floor. Fire broke out because of the mixing of these mutually reactive chemicals. Desks started to burn, but the fire was extinguished by the teachers and pupils at 1:20 p.m. 20, 37).

(ii) Beside this, although not reported as a fire, the ignition of yellow phosphorus occurred in a science room of a middle school 38).

The Tokachi Offshore Earthquake

(i) In the Tokachi Offshore Earthquake at 9:52 a.m. on May 16, 1968, a chemical fire occurred in the physics and chemistry preparation room on the second floor of the Misawa Commercial High School. The fire was caused chemicals falling in the preparation room that shifted when the building collapsed. Although the chemical shelf did not tip because it was fixed to the wall, the chemical containers fell off the shelf. This fire was extinguished by the staff using dry−chemical fire extinguishers [36].

(ii) At the Hachinohe−kita High School, during the earthquake the door of the chemical storehouse was pushed open after an explosive sound inside, and the gas blown out of the door ignited.

The chemical storehouse (3.3m ^{2}) was located at the corner of the chemistry preparation room, and the shelves holding the chemicals were arrayed in five layers in a L−form; chemicals were arranged in accordance with their classification. Metallic sodium, having been on the third layer, fell down, and hydrochloric acid and sulfuric acid also fell. Supposedly the fire was initiated in the chemical storehouse and the door pushed open by the pressure of gases resulting from combustion, which blew off the vaporized gases of ether, acetone and others, and eventually led to ignition when these gases mixed with air.

There was no retainer on the shelves to prevent the containers from falling. The bottles that fell down were 10 to 20% of the total stock, considerable numbers of bottles having been stacked on the shelves. The fire was immediately extinguished with powder fire extinguishers [36].

The Miyagi Offshore Earthquake

Many valuable records regarding the Miyagi Offshore Earthquake will become important resources for designing measures against earthquake hazards in the future.

(i) In the Miyagi Offshore Earthquake, fires occurred at two laboratories in the Tohoku Pharmacy College. At one of the laboratories, a group of about ten students was having a meeting of a reading circle with a professor. When the earthquake began, the professor supported the shelf on which the chemicals were stored with his hand to prevent its collapse.

According to a testimony by a student, bottles of chemicals continually dropped from the shelf toward the feet of the professor and produced balls of fire instantly. The professor suffered burns on his feet, and, realizing the danger of staying in the room, made all the people evacuate before he himself left the room [31].

(ii) At another chemical laboratory of the college, a solvent in a broken bottle ignited from a gas burner in use. The fire could not be extinguished by use of the fire extinguishers installed there [32].

(iii) There were several fires in the building of the Faculty of Science, Tohoku University. Three rooms −− 403, 410, and 705 −− were destroyed by fire because of the failure of the extinguishing system at the beginning of the quake. The causes of the fires were surmised to be as follows [33].

In room 403, a bottle containing ether with sodium (a drying agent) was placed in the lower level of a reagent shelf that was fixed to the wall. The bottle slid off the shelf because of the quake and fell to the floor. At the same instance, bottles containing a variety of inorganic reagents fell down and broke, some of which also hit and smashed the ether bottle. It was alleged that the sodium thus exposed reacted with aqueous reagents and ignited, which in turn ignited the spilled solvent and thereby caused a rapid expansion of the fire.

There were three students in the room who closed the main gas cocks immediately at the outbreak of the fire and worked to extinguish the fire with extinguishers. They also sought help by making others aware of the fire. Facing a dangerous situation, however, resulting from the rapid expansion of the fire and the smoke and gas generated by combustion and reaction of chemicals, they escaped following the instructions of the professor in charge.

In room 410 a fire was caused by the reaction of chemicals in a similar manner (the reaction of sodium with water as described in reference [35]), but it was extinguished by students in attendance. The students, after closing the windows and doors of the room, went out to help fight the fire in room 403.

When all the fires were extinguished, a brown smoke was still seen at ground level. When a fireman entered into the building to evaluate the scene and opened the window to look inside the heavily smoking room, reignition of the fire occurred [35] .

Regarding this fire, it has been said that, considering the fire involved sodium, too much time was spent after the arrival of the fire engine before a water spray was started. Prohibiting water–spray can lead to the expansion of a fire unless other measures are taken. As to the handling sodium in a chemical experiment room, the amount of sodium stored should be limited to the minimum amount required, and that should be less than the amount that would produce any problem during water–spraying by firemen.

In the room 705, the distillation of a high–boiling alcohol (diisopropyl benzyl alcohol) on an oil bath was being carried out, and the vibration caused to the oil bath to tip. At the same time many bottles of organic reagents fell, broke, and leaked, supposedly causing ether, benzene and methanol to ignite. The researchers, teaching assistants and students present tried to extinguish the fire but had to withdraw because of the dangerous situation presented by the vigorous generation of gases. The record of words describing the situation was spoken with regret: "We decided to retreat when we were told that the fourth floor was burning, for we would have continued to fight the fire in front of us if it had been the only fire".

(iv) In the Faculty of Medical Science, a bottle of chromium trioxide broke to scatter the contents over the floor. Although picked up quickly, the chromium trioxide mixed with other reagents and caught fire but was fortunately brought under control with the help of many people [35] . On the sixth floor of a building, a shelf with a support to protect against vibration fell down because of the flexing of the support bar, which caused the scattering of 500g of chromium trioxide over the floor. While the chemical was being recovered, tiles began to swell and eventually a fire broke out, which was extinguished after scorching an area of only 1m^2, [33] .

(v) In an experiment room, a bottle containing pieces of metallic sodium fell down on the floor and broke. Water was present, and a pillar of flame shot up in a second. When all flammable things in the area had been consumed, the fire ceased to burn, leaving only the immediate surroundings scorched (32) .

(vi) On an experiment table in a room, a small bottle from an upper shelf fell on a flask containing a little tetrahydrofuran and metallic lithium. Both the flask and the bottle were broken and a flame shot out caused by the reaction of the lithium with water that had leaked from a thermostat at the corner of the table. Combating the fire with extinguishers was not very effective, and the fire was ultimately brought under control only after all the extinguishers placed nearby were used (32) .

The Whittier Narrows Earthquake

At 7:42 a.m. on October 1, 1987, an earthquake occurred of magnitude 5.9 with its seismic center at the Whittier Narrows district,14 miles east of downtown Los Angels; it caused considerable damage. The casualties were 7 dead and 1,135 injured, and the total damage amounted to over 200 million dollars for the city and county of Los Angeles (52) .

On that day, the Los Angels Fire Defense Department received 155 fire reports, among which 61 (39.3%) were of building fires, 26 (16.7%) of automobile fires, and 15 (9.6%) of garbage fires.

Fires directly caused by the earthquake were six in number, one of which, in a laboratory at the University of California, was started by a fire of leaking toluene ignited either by an electric furnace or from the reaction of metallic sodium. The total damage amounted to 24,000 dollars.

Table 2.4 Chemical fires in laboratories in the Great Kanto Earthquake

Destruction by fire
Chemical storehouse in drug plant of the Meguro Medical Supplies Depot
The Medical Supplies Depot of the Army
The research laboratory of the Nippon Junyaku Co., an alloy maker
Small fires
The Commerce and Industry Promotion Office of Tokyo−fu
The Institute of Physical and Chemical Research (two places)
The Mitsuwa Laboratory
The Tokyo Institute of Hygienic Sciences (two places)
The Industrial Research Institute of the Ministry of Agriculture and Commerce
The Nitrogen Research Institute

b. Laboratories and experiment rooms

The Great Kanto Earthquake

There are records of places having fires as shown in Table 2.4, although a slightly different places are indicated in other references [15, 16, 30]. None of the stories of the fires are known.

The Fukui Earthquake

(i) There was a fire at the agricultural experiment station of the prefecture, burning three buildings and a house. The fire was not spread into the surrounding area because it was an independent facility.

The Niigata Earthquake

(i) In the laboratory of the Niigata Second Plant, Mitsubishi Metal, glass bottles of ether (500cm ^{3}, 2 bottles), benzene(500cm ^{3}, 1 bottle), oils(5 bottles), and others flammables were tipped and dropped by the earthquake and caught fire, resulting in the burning of the instruments in the room. The fire was extinguished by the employees at 1:12 p.m. [37, 39].

The Miyagi Offshore Earthquake

(i) From a chemical storage room in the Hygienic Experimental Station of Miyagi Prefecture, a liquid spewed out of its container and reacted to produce black smoke along with an offensive and irritating odor that filled the interior of the building. The fire was put out in about twenty minutes using extinguishers and water [47].

(ii) In the Industrial Technology Center of Miyagi Prefecture, a bottle of concentrated sulfuric acid was broken and caused a fire when the acid came into contact with filter paper, but the fire was immediately extinguished [48].

Other earthquakes

(i) At about 7:45 p.m. on July 1, 1968, there was a strong earthquake in Tokyo, with a seismic intensity of 4 and the magnitude of 6.4. In this earthquake, in an experiment room on the second story of a company in Ota−ku, large quantities of chemicals that were on shelves or on the floor fell down or tipped over to cause a fire, supposedly started by the mixing of mutually reactive chemicals. The second story part of the building (45m ^{2}) was destroyed and one person was slightly injured [39].

c. Pharmacies

The Great Kanto Earthquake

Three places, namely, a drug store, a pharmacy, and a drug supplier, caught fire and were destroyed. Beside these, chemicals caught fire at Kasuga Pharmacy, the Shinagawa Plant of Sankyo Drug, the drug maker Walterpet, and Inagaki Apothecary, but these fires were immediately extinguished [15, 30].

The Fukui Earthquake

There are no records of fires in pharmacies and the like.

The Tokachi Offshore Earthquake

(i) In a storage room of a pharmacy at Mikka−cho, Hachinohe City, a leaking chemical caught fire, resulting in destruction of three buildings. When the earthquake started, a liquid was dropped onto a table from near the middle of the ceiling (a point located just below the storage room at the mezzanine) of the first story office.

Five minutes after the outbreak of the earthquake,the veneer ceiling turned black, generated white smoke at several points, and soon caught fire. The fire services office together with the local fire defense brigade made effort to stop the fire, but, because the hydraulic pressure was only half of the normal, the fire could only be extinguished two hours later by using three water pools.

It was estimated that the chemicals stored in the room on the mezzanine fell down and and broke, releasing strong acids which then generated heat. When ethanol, methanol, benzene, and other flammable organic liquids mixed in, they caught fire. The chemicals stored there at that time were reported and are listed in Table 2.5 [36].

Table 2.5 Chemicals placed in the storehouse

Name of chemicals	Contents of bottle in g	Number of bottles
Hydrochloric acid	500	80
Sulfuric acid	500	20
Benzene	500	60
Benzene	100	100
Methanol	500	30
Ethanol	500	50
Ethanol	100	100
Oxidol	500	100
Glycerine	500	50
Glycerine	100	100
Cresol	500	50
Cresol	100	30
Glacial acetic acid	500	80
Amyl acetate	500	30
Chlorinated lime	500	20
Strong ammonia water	500	80

(ii) At a pharmacy at Chuo−cho, Misawa City, bottles of chemicals dropped from the display shelf to break and burn, probably from ignition caused by the mixing of mutually reactive chemicals. The chemicals stored at that time are reported in Table 2.6.

Table 2.6 Chemicals that were stored

Name of chemicals	Contents of bottle in g	Number of bottles
Hydrochloric acid	500	12
Sulfuric acid	500	3
Nitric acid	500	3
"A" benzene	500	25
Methanol	500	6
Acetone	500	2
Lacquer thinner	250	20
Alcohol for sterilization	500	6
Thinner	1.8[l]	6
Oxidol		
Potssium bichromate	500	2
Potassium permanganate	500	1
Ether	500	2

d. Hospitals and doctors' offices

The Great Kanto Earthquake

(i) It is recorded that there was one chemical fire in the medical room of a doctor's office and in a dentist's office 16, 30) . They were extinguished immediately.

(ii) It is recorded that there were several chemical fires in university hospitals 16, 30) .

e. Plants

There are records of chemical fires in plants such as: a plant of Hakubunkan (small fire), a plate-making and printing plant (destroyed), and a plant making celluloid (destroyed) in the Great Kanto Earthquake; and a plant of Fukui Newspaper (destroyed), and an oil plant (destroyed) in the Fukui Earthquake.

f. Others

In addition to the above, cases are known of a chemical fire at Takanawa-Gosho (destroyed) caused by the spilling of hydrochloric acid bottles (small fire) in the Great Kanto Earthquake, and at a paint shop (destroyed) in the Fukui Earthquake.

2.5.1.3 Oil stoves and oil ranges

Fires from oil stoves and oil ranges were recorded in the Tokachi Offshore Earthquake 36) in 1963 and in the Ebino Earthquake 39) in 1968. In the Tokachi Offshore Earthquake, 20 fires from oil stoves plus 8 fires from oil ranges accounted for about

50% of the total 50 fires. The specific causes of these fires are summarized in Table 2.7.

Table 2.7 Causes of fires from hazardous goods in the Tokachi Offshore Earthquake.
(1) Oil stove

Cause	Number of cases
Tumbling	
Independent tipping	2
Tipping induced by contact with another article	6
Tipping caused by a stumbling man	1
Dropped by a man	1
Unknown cause	2
Tilting caused by a tumbling of other article	1
Swaying caused by the vibration	1
Dropping of other flammable articles on the stove (paint or paper)	2
Tipping of the oil tank of a pot-type oil stove	1
Unknown cause	3
Total	20

(2) Oil kitchen range

Cause	Number of cases
Colliding with a small boiler	2
Colliding with a towel steamer	2
Dropping from a cooking table	3
Unknown cause	1
Total	8

It was shown that the places these fires from oil stoves and the like occurred were not scattered all over the city but were concentrated in areas where the ground was weak.

As to the types of houses that burned, generally fires in homes and houses combined with shops were more frequent. Among 20 fires from oil stoves, four resulted in complete destruction, three in half destruction, and thirteen in small, partial burning, the majority of fires having been extinguished immediately after they broke out.

As can be seen in the table, 12 cases of fires from oil stoves were caused by the stoves tipping over; cases of simple tipping (by earthquake vibration) were only two, and others were ignited by stoves tipping or colliding with other objects. It is understandable that articles placed around oil stoves influence fires caused by them.

Regarding 20 cases of oil stove fires, people turned off the stove before seeking refuge in 7 cases, the stove was left to burn in 8 cases, and no information was available in the 5 remaining cases. It is worth remembering that there was a case where the stove was initially turned off, but because the fire did not go out immediately a large fire was started later when the stove tipped over.

In the Ebino Earthquake on February 21, 1968, one of the guests who were surrounding an oil stove in a hotel jumped out of the room at the outbreak of the second after-shock, knocking the stove over and thereby setting the wall on fire. It was fortunate that the fire remained a small one and was immediately extinguished 39) .

2.5.1.4 Oil pans

It is recorded that fires from oil pans occurred six times (complete destruction) in the Great Kanto Earthquake and once in the Niigata Earthquake.

2.5.1.5 Oil tanks and attached facilities

Fires of oil tanks in earthquakes occurred, nationwide and worldwide, and are listed in Table 2.8. Many of them were of crude oil, but others included cases of heavy oil and gasoline.

Identified as the specific causes of the ignition were: sparks from percussion or friction from floating roofs or other objects (3 cases), ignition of leaked oil by an open flame (2), ignition of leaked oil from an automobile engine (1), and a flame spread from another source (1).

Table 2.8 Fires of tanks and attached facilities in earthquakes.

(1) Oil tank

Name of earthquake	Type of flammable substance	Source of ignition
Great Kanto	Heavy oil	Open fire
Niigata (the first fire)	Crude oil	Hitting and friction of floating roofs
Niigata(the second fire)	Crude oil	Spreaded fire
Niigata (the fire at a distillery)	Heavy oil	Open fire
Niigata (the fire of a broken underground conduit)	Crude oil	Automobile engine
Middle Japan Sea	Crude oil	Sparks from hitting and friction of floating roofs
Alaska	Gasoline etc.	Sparks from hitting and friction

(2) Gas tank

Name of earthquake	Type of flammable substance	Source of ignition
Middle Miyagi	City gas	Hitting and friction by broken tanks
Taft	Liquid butane	Sparks from a transformer

a. Domestic

The Great Kanto Earthquake

(i) In the Great Kanto Earthquake on September 1,1923,a fire occurred among the Navy's heavy oil tanks located midslope at Hakozakiyama, Yokosuka City. The total capacity was about 100,000t, each tank holding about 6,000t. The earthquake caused the heavy oil that almost completely filled the steel tanks to slosh and to create a great noise by hitting the roof plates. The roof plates were partly destroyed, so that the oil began to flow intermittently down the outside walls of the tanks like waterfalls. The splashing oil spread over the surroundings like a fog.

This oil mist caught fire by contacting either a flame on a water heater or the flame of a bellows heating coke for steel plate riveting. Beside the oil spill from the roof, oil flowed from ruptures of the outlet and inlet pipes at the bottom of the tanks. Huge quantities of burning oil rushed down the slope into the naval port. The warships anchored in the port withdrew hurriedly. Based on this experience, circular tanks were constructed and buried in the ground to replace the steel tanks that were ruptured 40).

The Niigata Earthquake

(i) The first fire in the Niigata Earthquake 37)

Just after the beginning of the earthquake on June 16, 1964 at 1:02 p.m. at the crude−oil tank yard on the premises of the new plant of the Niigata Refinery, Showa Petroleum Company(4914 Numadare, Niigata City), five crude−oil tanks caught fire almost simultaneously because of the motion of their floating roofs. Retaining dikes had been broken by the earthquake, and the spilled oil spread the fire to 20 homes south−east of the refinery, burning an area up to 97,700m ^{2} in size. One tank continued to burn to the end, some 15 days later; the complete extinguishing of the fire was achieved at 5:00 a.m. on July 1.

Immediately after the initial earthquake vibration, the contents of the tanks began to slosh back and forth and to spill out from the gaps between the floating roofs and the side plates and flow down the outside walls. According to the story of the witnesses at the scene, the first tank to ignite was No.1103, but almost simultaneously all five tanks caught fire and the whole tank yard was covered with flame. This was the beginning of the first fire, whose black smoke covered the sky and created a gruesome scene. The cause of the ignition was thought to have been the collision and friction between the floating roofs on the tanks. One of the witnesses said, "The floating roof of the No.1103 tank in front of me jumped up three or four times, after which flames rose up along the outer wall and black smoke covered everything in the area. In that instance, I felt a strong radiative heat."

The foam-type non-movable extinguishers installed at each crude oil tank could not be used because the water supply had failed, and the fire engines approaching the site were hindered by the cracks on the road surface and flooding on roads. One fire engine was able to arrive at the scene only at about 5:00 p.m. At about 6:00 p.m. of the same day, a second fire occurred at the old plant about 300m north of the new plant, and fire fighters therefore were forced to confront a gigantic fire extending over the whole refinery.

(ii) The second fire in the Niigata Earthquake [37)]

At 6:00 p.m., about five hours after the outbreak of the earthquake, a fire accompanied by an explosion occurred near the border between the Niigata Refinery of Showa Petroleum Company and the Niigata First Plant of Mitsubishi Metal Company (Numadare, Niigata City). The fire destroyed both plants and spread to the Niigata Tankage of Asia Petroleum Company and the Niigata Edible Oil Industries, both located in the adjoining lot to the west, and also to about 300 homes in Konan-cho, all of which were destroyed. The fire was brought under control at 5:00 p.m. on June 20, five days after the start of the fire. An area totaling 235,000m ^{2} was destroyed.

According to Kitagawa, a pile of reduced iron powder was inundated with sea water and generated a large quantity of heat. The pile collapsed, producing a steam explosion, which in turn ignited a gasoline spill that developed into the second fire.

(iii) The fire of a heavy oil tank at a distillery [37)]

At the distillery of Narusawa Petroleum Co.(Matsushima, Niigata City), a 100m ^{3} fuel tank containing about 80m ^{3} of heavy oil dropped from its rack and caused a fire when the heavy oil ran into the boiler. The fire engines arrived too late, again because of damaged roads and flooding, and 14 buildings were consumed in the blaze. The fire was put under control at about 4:00 p.m. on the next day, the 17th.

(iv) Fire of an underground conduit for crude oil [37)]

An underground conduit for crude oil to the Ose Tankage of Japan Petroleum Co. cracked in the earthquake, causing the oil to leak to the surface of a road. An automobile passing nearby at 1:17 p.m. fell into a hole, and when its engine was restarted in an attempt to get out, the leaked oil caught fire. After destroying the storehouse of the Niigata Plant of Nitto Spinning Co. and an estimated 11 nearby homes, the fire was extinguished at about 8:30 p.m. on the 19th. The underground conduit had cracked at the point where it had been welded where it crossed a Hume pipe for the wastewater stream of the plant.

The Middle Japan Sea Earthquake

(i) At 0:00 p.m. on May 26, 1983, an earthquake 7.7 in magnitude with its seismic center offshore at Noshiro, Akita Prefecture, occurred, and a fire broke out at a crude oil tank (outdoor storage) in the Akita Power Generation Plant of Tohoku Electric Power at Ijima, Akita City. The fire fortunately never developed into a major blaze and was extinguished in 28 minutes by the activities of 10 municipal fire engines and five fire engines from civil−defense brigades.

The tank that caught fire was of a floating roof type; it was alleged that the floating roof swayed from a vibration during the earthquake and produced sparks by hitting the spraying pipes at the upper part of the tank. These sparks ignited the vapor of the crude oil. The fire was contained in the region over the floating roof and resulted in the loss of about 20m^3 of crude oil and damage to the weather shield and tube seals.

Several tanks were discovered that had some leakage of oil but did not cause a fire. It was estimated that a longer cycle vibration lasting for a longer period of time produced sloshing of the oil and hence leakage. It was also found that the impact of oil on the roof produced by sloshing can destroy the roof 28).

b. Overseas

The Alaska Earthquake

(i) On May 27, 1964, historically the greatest earthquake that has occurred in the east−southeast of Anchorage, Alaska, was recorded with the magnitude 8.4. Oil tanks in four areas within 150km of the seismic center suffered great damage. The damage by this earthquake was characterized by the fact that fires took place in three of the four areas.

Tanks in the Whittier area suffered great damage from the seismic wave (Fig.2.2). A witness who tried to escape by car crossed the tank yard about one minute after the start of the earthquake when the top of a 53,500bbl capacity gasoline tank broke and the contents blew out. Fearful that the car would catch fire, he left the car and ran to the exit. Just as he left the tank yard, the seismic wave came and the explosion occurred 43).

The rupture of the top of the gasoline tank caused the contents to be blown out and explode, and four tanks (2 for gasoline, 1 for kerosene, and 1 for diesel oil) caught fire. Eleven tanks were moved by the seismic wave, most irreparably damaged 42).

(ii) In the Valdez area there were three tanks, large and small, and one tall one tipped over and caused a fire 42).

(iii) In the Seward area there were more than thirty tanks, and the tanks owned by

Texaco were involved in fires [42] .

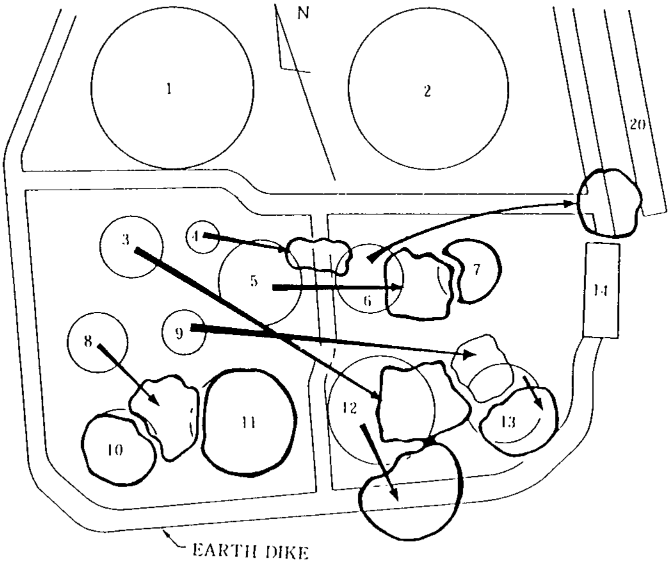

Fig 2.2 Great damage of oil tanks in Whittier area(Alaska earthquake [41])

2.5.1.6 Gas tanks

Earthquakes caused fires of gas tanks in the Miyagi Offshore Earthquake and the Taft Earthquake in the U.S.A. as shown in Table 2.8. The one in Miyagi was caused by the leakage of city gas from a broken wet gas holder, followed by the ignition of the gas by sparks from collisions of falling supporting pillars. The fire in Taft was caused by the leakage of butane gas from a broken spherical tank, followed by the ignition of the leaked gas caused by sparks produced in a transformer during the aftershock [43] .
Among 14 liquefied propane gas tanks installed in the Paroma cycling plant, five were spherical tanks 30 feet in diameter. Two that were nearly full tipped over, 3 and 6 inches diameter pipes burst, and an explosion occurred three minutes later. The detonation spread over an area of 270 × 360m [42] .

2.5.1.7 Propane gas bomb

The Niigata Earthquake

(i) A propane container with a capacity of 50kg tipped over because the earthquake broke a rubber tube, after which the gas blew out and caught fire [37] .

The Tokachi Offshore Earthquake

(i) It was reported that two propane gas bombs with a capacity of 50kg each collided with each other during the earthquake, resulting in the ignition of gas that leaked out by sparks from the collision [36]. However, it is doubtful and remains to be proven that the sparks produced by the collision of bombs in an earthquake can ignite propane gas.

2.5.1.8 Industrial furnace

Fires from industrial furnaces occurred in the Fukui Earthquake and the Tokachi Offshore Earthquake.

The Tokachi Offshore Earthquake

(i) In Hachinohe City, Aomori, a fire was caused by the heater of a drying furnace of a marine product processor. The details reported were: a heat-protecting pile of bricks in front of the fire door of a drier, a rotary kiln type with a rotating iron cylinder 18m in length, collapsed in the earthquake causing the vinyl chloride pipe (1.5cm diameter) connecting the heavy oil burner to melt. The heavy oil that escaped from the melted pipe caught fire when it came into contact with the overheated bricks [36].

2.5.1.9 Gas appliance and gas piping

a. Domestic

Fires from gas appliances took place in the Great Kanto Earthquake (9 cases), the Tokachi Offshore Earthquake (1 case), and the Urakawa Offshore Earthquake (1 case).

The Tokachi Offshore Earthquake

(i) A gas range with an automatic lighter fell from the cooking table of a kitchen during the earthquake when the lever of the automatic lighter was moved to ignite the gas. The resultant fire was extinguished by a bucket brigade of nearby residents who doused the fire with water [39].

The Urakawa Offshore Earthquake

(i) At 0:04 p.m. in the Urakawa Offshore Earthquake in Tomakomai City, a fire was started by a gas rice-cooker but was immediately extinguished by the nearby residents. The earthquake had occurred while the family was out. A plastic chopping board had fallen, hitting the gas rice-cooker, and causing the pot and range to separate, thereby exposing the pilot light. It was assumed that the plastic chopping board, being heated by the pilot flame, was overheated and ignited [44].

2.5.1.10 Matches

There were known fires caused by the falling of matches in the Fukui Earthquake (1 case), the Miyagi Offshore Earthquake (1 case),and the Middle Japan Sea Earthquake (1 case).

2.5.1.11 Explosives

Only two cases worldwide of fires caused by explosives during earthquake were reported.

The Great Kanto Earthquake
(i) At the gun cotton drying place in the First Plant of the Second Navy's Explosive Depot in Hiratsuka City, Kanagawa, 4,500kg of gun cotton (nitrocellulose) that was being dried ended up under a building destroyed by the earthquake. The nitrocellulose caught fire because of friction among the structural components during the collapse of the building [39].
(ii) Explosives at the working department of the Army's Technical School caught fire, destroying two buildings [30].

2.5.2 Hazardous goods causing damages other than fires in the past earthquakes

2.5.2.1 Oil leakage

Several cases of oil tank fires in earthquakes have occurred, including the case in the Niigata Earthquake, as described in section 2.5.1.5. In some of the cases leaking oil was ignited, but many cases are known in which oil leaks luckily did not lead to a fire. Oil leakage not only increases the potential danger of fire but also may be responsible for great damage to the environment.

The accidental destruction of oil tanks at the Sendai Refinery of Tohoku Petroleum Co. in the Miyagi Offshore Earthquake, although fire did not break out, caused the second greatest amount of damage next to that in the Niigata Earthquake in the Japanese oil complexes. A huge amount of oil spilled on the land and into the sea. Chisaki [42] described the scene of this oil leakage as follows.

Almost simultaneously with the outbreak of the earthquake, three oil tanks inside the collective dike(capacity of 34,000m^3) at the northeast of the refinery were broken near their bottom plates, and almost all (70,000m^3) of the topped crude and the vacuum gas oil in storage instantaneously spilled out of the tanks. The leaked oil overflowed the dyke and at the same time dug out the base of the dike causing the flooding of the oil into the premises. Thus, the area flooded by the oil covered most of the lanes and unoccupied grounds of the refinery, in a depth at some times reaching more than 50−60cm at places where the ground level was low.

Most of the flooded oil in the premises remained in the refinery, retained by the dikes there for flood prevention, but part of the oil that came through storm drains into the guard basin flooded out over the sea bypassing the gaps of dampers and drainage pipes.The refinery immediately extended oil−fences to prevent the further extension of the oil spill, and almost all leaked oil was recovered in a week.

Chisaki [42] and Nakakuki [40] summarized other earthquake disasters in oil complexes. Table 2.9 lists accidents of oil leakage along with the others.

Table 2.9 Accidents of oil tank leaks in earthquakes [40, 42].

Name of earthquake	Date	Country	A mount of leaked oil(m^3)
Long Beach	3/10/1933	U.S.A.	7,300
Taft	7/21/1952	U.S.A.	240
Alaska	3/27/1964	U.S.A.	---
Niigata	6/16/1964	Japan	---
Concon	3/28/1965	Chile	---
Tokachi Offshore	5/16/1968	Japan	---
San Fernando	2/9/1971	U.S.A.	1,000(water)
Lima	10/3/1974	Peru	9,500
Miyagi Offshore	6/12/1978	Japan	70,000

2.5.2.2 Leakage of fuel gas

In the past great earthquakes, cases of leakage of city gas and liquefied propane gas occurred, but cases involving fires were relatively rare in Japan. This was supposedly due to the small scale of most of the leaks and to success in removing the ignition sources.

In the recent Mexico City Earthquake (September 19, 1985) and the Whittier Narrows Earthquake (October 1, 1987), however, there were many gas fires caused by gas leakage and subsequent ignition.

2.5.2.3 Leakage or generation of toxic substance

In chemical laboratories or similar facilities at the time of an earthquake, chemicals may leak that produce an irritating or corrosive gas. For instance it was reported that, in the Miyagi Offshore Earthquake in a chemical laboratory of the Prefectural Sendai Technical High School, a bottle containing an acid dropped from a table and filled the room with an odor so irritating that people could not enter the room [46]. It was also reported that, in a chemistry lecture room of Tohoku University, vapors of pyridine and tetrahydrofuran filled the room to the extent that restoration work could not be started until two days after the earthquake [35].

In the Middle Japan Sea Earthquake, there were no chemical fires, but the destruction of a bottle of a chemical in a school was reported [49]. In the Noshiro Technical High School, Akita Prefecture, no chemical fire occurred, but a 18,000cm^3 bottle of sulfuric acid in the chemical storehouse in the science room was broken. Although the acid was immediately neutralized, the concrete floor was corroded [50].

As described in section 2.5.1.2, schools, laboratories, pharmacies, hospitals, and doctors' offices generally store numerous chemicals, many of which are have a possibility of either generating a toxic vapor or mist if the bottles are damaged, or producing a toxic substance through their reaction with other substances. In past earthquakes, however, no casualties have been reported through accidents of these types.

2.6 Accidents Involving Pyrotechnics

Among accidents involving pyrotechnics in the past, one with fireworks will be described here as an instructive example [54] .

a. Development of the fire

At 1:59 p.m. on August 14, an emergency call for an outbreak of a fire was made to the Hachinoe Fire Services Office. Two fire engines from the same branch office were promptly dispatched to the scene to fight the fire, and additional six engines were sent to the spot later.

At 2:07 p.m. an ambulance arrived for relief, but, because of the large number of injured, three ambulances in total came to provide relief, first–aid, and transport to the hospital.

It was recorded that the fire was suppressed at 2:05 p.m. and was extinguished at 2:25 p.m.

According to several information sources including newspapers, students were playing with setting off a ball–type firework at the front of a shop when the fireworks displayed there ignited and rapidly exploded. The fire spread so widely in under a minute that the entrance to the shop was blocked, confining many children and students in the shop.

About 23 children were thought to have been the shop, several of whom probably rushed out of the shop through the entrance at the outbreak of the fire, but others were confined inside, their exit hampered by the flame and smoke.

The shop was engaged in the business of operating game machines and a lunchroom, and in selling stationery, miscellaneous goods, and toy fireworks as seasonal items. The arrangement of goods in the shop was reported as illustrated in Fig.2.3.

The shop owners, who had suffered a nighttime robbery prior to the fireworks accident, had taken the countermeasures of both locking the back door and also putting iron bars on the door, as well as installing wooden bars on the side window. This was the major factor confining the students inside; most of them had to escape through the window by breaking the wooden bars.

b. Casualties

According to the initial survey by the Hachinohe Fire Services Office, the casualties in the fire included 17 injured, 16 males and 1 female; 3 were severely injured, 6 moderately, and 8 lightly. In terms of ages the breakdown was 1 pre-school child, 1 elementary school pupil, 7 middle school pupils, and 8 high school students. Two severely injured children were critical, incapable of breathing on their own. One lightly injured pupil became worse afterward, was eventually classified as severely injured, and was moved from the Surgical Taneichi Hospital to the Municipal Hospital.

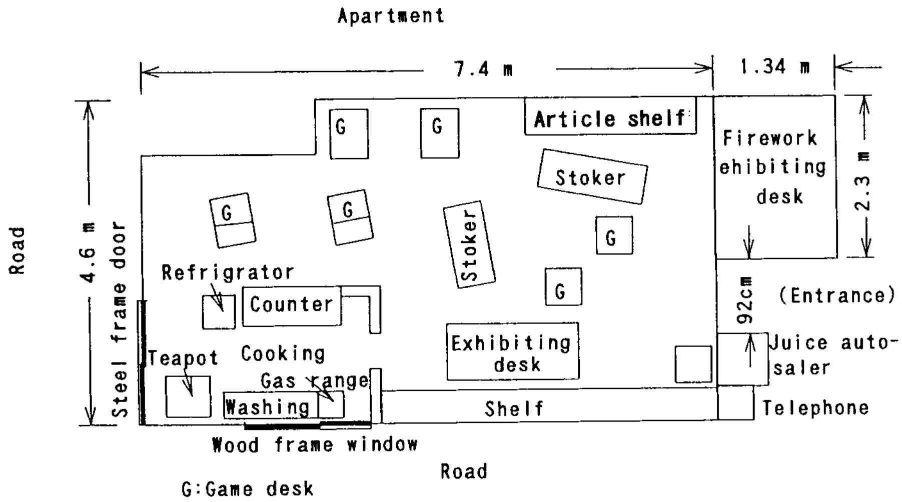

Fig. 2.3 Fire field of toy fireworks shop

Sixteen among the 17 injured were transferred to three hospitals in the city by ambulances; 5 (3 severely injured, 2 lightly injured) to the Workmen's Accident Hospital in Aomori City, 6 (all moderately injured) to the Municipal Hospital of Hachinohe, and 5 (all lightly injured) to the Taneichi Surgical Hospital. One lightly injured child went to a hospital by himself. One of these persons died in December of the year.

Their injuries were inhalation burns, presumably caused by breathing in the hot smoke produced by the burning of the toy fireworks. In view of the observed increase of carboxyhemoglobin observed in their blood, inhalation of carbon monoxide also probably occurred. The appearance of soot on forcibly exhaling suggested the inhalation of a considerable amount of smoke as well.

According to a comment by the ambulance team, the symptoms of the moderately and lightly injured (11 persons) were: larynx pain for 7, burns for 7 (on ear, shoulder, elbow, face, neck, arm, hand and others), and eye pain for one.

When the fire defense brigade arrived, one person was lying on his back with burns on his face, hands, and arms. Immediately a search was made inside the shop, and it was confirmed that no one was left inside unable to escape. Other persons who were burned were outdoors taking positions as shown in Fig.2.4.

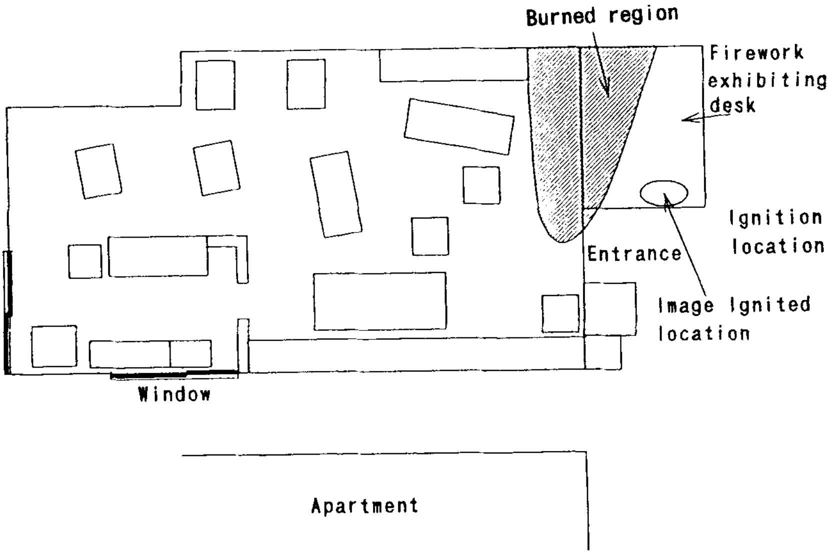

Fig. 2.4 The location of injuried persons when fire cars arrived

c. Damage to the property

The scorched area is shown as a hatched range in Fig.2.4, corresponding to a size of about 5m ^{2} . The Hachinohe Police Office reported that property damaged by the fire included: the inside wall (made of fire−resistant board) on the side of the room facing the road, the ceiling (made of fire−resistant board), the floor (about 1m ^{2}), and pillars and the roof of the entrance.

d. Duration and violence of the burning of fireworks

According to the report by the firemen who first arrived at the scene, the fire was nearly suppressed thanks to the initial action of the nearby residents. The fire was extinguished 2 minutes after the fire engine arrived at 2:03 p.m.

The time needed for the reception of an emergency telephone call from the outbreak of a fire has generally been said to be about one minute. The call in this case was supposed to have been made within that amount of time. Under this assumption, the outbreak of the fire was at 1:57−1:58 p.m., and the suppression was at 2:05 p.m.; hence, the time the fireworks actually burned was about 7−8 minutes.

The time between the ignition of the fireworks and the existence of a violent fire has not yet been concluded. Some said that the fire expanded in several seconds, whereas others maintained that it it took one minute. Some people confined in the shop said that the sound of the fireworks was considerable, not like that of crackers but rather like that of skyrockets.

Because of the ignition of the fireworks on display in front of the shop, only few people could escape through the entrance, leaving 17 or more people behind in the shop. The fire must have spread very rapidly and have been accompanied by very vigorous burning. On the other hand, the fact that about half the people confined inside suffered external burns and the property damage outside near the entrance was limited suggests that fireballs ejected from the fireworks reached the people inside but not outside.

Thus far neither a report that someone is hearing was impaired by the explosion nor a report that window glass plates were broken by the blast has been filed.

The arrangement of the fireworks on the display counter was as illustrated in Fig.2.5, according to the memory of the victims. It can be estimated that the ignition of a firework played at position "A" could ignite a firework on the display counter nearby, and the resulting fire, spreading from left to right, would quickly become a conflagration.

The fireworks were being displayed uncovered in small boxes. Selling fireworks by making a display on a counter in front of a shop seems to have represented the typical way of firework were sold in Hachinohe City. During an inspection tour, several shops all with this type of display were noticed on the street.

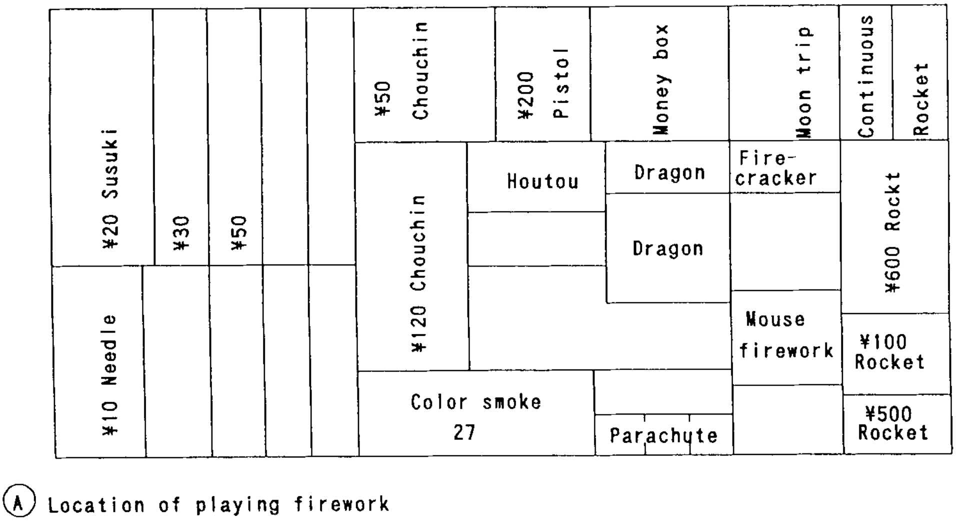

Fig 2.5 Arrangement of fireworks on exhibiting desks (recollection of witnesses)

e. Factors compounding the damage

This accident proceeded in the following steps:

(i) Lighting a firework close to the display counter.

(ii) Ignition of a firework on the display counter.

(iii) Rapid spread of fire among fireworks on the display counter.
(iv) Many people in the shop.
(v) Escape through the entrance difficult because of vigorous burning of fireworks.
(vi) Closed and barred back door (iron bars) and the window (wooden bars).
(vii) Inhalation burns caused by the smoke that filled the shop.
(viii) "Stars" and "rockets" on fire inside the shop, burned many.
(ix) Escape via window after breaking wooden bars in seven minutes, before the arrival of the fire defense brigade.
(x) Serious inhalation burns make some victims incapable of breathing.
(xi) Fire brigade summoned ambulances, administered first aid.
(xii) Ambulances arrived and transported the injured to hospitals.
(xiii) Treatment in hospitals.
(ixv) Investigation of the causes by the police.

(i), (ii) Accidents of this type, in spite of prohibitions, have occurred several times every year. It is said, however, that no cases have resulted in injury or death; this may mean that there have been no cases like this situation in which people near the accident were confined, cut off from escape, and suffocated by smoke.

(iii) The rapid spreading of the fire of the fireworks displayed was a matter that cannot be predicted even by the authors. The spreading was so rapid and the burning was so vigorous that only a few people could escape through the entrance immediately after the outbreak of the fire.

(iv) There were many people in the narrow shop when the fire broke out (23 children and pupils playing games or eating lunches). They were panicked by the fire so that only 5–6 people could escape through the entrance while the fire was still relatively small.

(v) Because of the vigorous burning (at least the people confined inside must have felt so) after the overall spread of the fire, the people could not escape through the entrance.

(vi) In the innermost side of the shop, there was a back door which was locked and fitted with iron bars for protection against theft. For the same reason the window at the back of the cooking table was fitted with wooden bars.

(vii) When many people were confined inside, the smoke from the fireworks filled the room and caused about half of the people to suffer inhalation burns. Evidence indicates that they inhaled soot and carbon monoxide produced by incomplete combustion. The degrees of these injuries differed depending of the hiding places the people found inside in efforts to avoid the fire.

(viii) The intensity of fire on the display counter was thought to be not great in view of the limited spread of the fire to the surroundings. Despite this, many suffered burns, supposedly caused by the flames of the fireworks, "stars" and "rockets", that shot into the room; the flames and the explosion must have terrified the people confined inside and inhibited their ability to escape.

(ix) The time available to escape was at the most about seven minutes. Finding that the back door was unavailable as an escape route, people broke the glass plates of the window behind the cooking table, broke the wooden bars, and escaped outside.

(iii), (v) Toy fireworks are sold generally at shop fronts. The conditions under which they will burn should be confirmed by experiments in situations like those in unexpected accidental fires. One could certainly make a case for developing fireworks that would retain the same pyrotechnic effects but would be slow at spreading fires.

In this accident the spread of the fire was surprisingly rapid. One of the reasons for this may be that an explosive substance leaked from a firework and coated its exterior, resulting in the an accelerated rate of burning and hence spreading the fire.

Pieces cut from a sheet of detonator paper for games were kept in a box, and when they were taken out they ignited and and injured a person. Explosive pieces that ignited upon being dropped were thought to have been ignited by friction.

(vi) When exits, entrances, and windows are fortified against criminal entry, measures should be so that their function emergency exits will not be impaired.

f. Measures based on lessons from this accident

This accident, although it was highly circumstantial with an array of bad conditions, made a tremendous impact on the people involved. They immediately took the following measures; 100,000 demanding letters and the sign shown below were provided and distributed to sellers of toy fireworks.

Dear Sellers of Fireworks :

PLEASE BE CAREFUL!

There was an accidental fire last summer as reported in the newspaper article attached herewith, which resulted 17 injuries, some of which were serious. Three high school students were seriously wounded, and one of them unfortunately died on December 1.

Such a tragic mishap was caused first by middle-school pupils playing with fireworks close to the fireworks display counter, and secondly by the unavailability of an emergency exit, the back door, because it had been closed and barred to protect against possible robbery.

Please take precautions as follows to prevent this kind of accident.

1. Please post the signs "No Fire" at firework display counters and other appropriate places.
   (Ask wholesalers for the signs, 45 × 21cm.)
2. Please seriously consider the position of each counter, and provide an emergency exit for escape in case of accident.
3. Please be careful and keep alert; do not overlook anyone lighting a firework in the shop front for whatever reason.

JAPAN FIREWORKS ASSOCIATION
4-2, Kyobashi-3-chome, Chuo-ku, Tokyo
Nisshin Bldg. 7 Fl.
Tel. 03-281-9871

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Chapter 3

EXPERIMENTAL EVALUATION OF FIRE AND EXPLOSION HAZARDS OF REACTIVE SUBSTANCES

3.1 Introduction

Experimental evaluation is essential for highly reliable assessment of the fire and explosion hazards from reactive substances. Much work has been done concerning the methods of such evaluation[1-6]. From among these methods, the best and most practical were introduced in the previous book[1].

The authors have proceeded with further study and have consequently found even better techniques of evaluation and analysis. These techniques will be described here. Of the methods referred to in the previous book, unchanged ones are not included herein.

Techniques considered by the authors to be useful and practical are summarized in Table 3.1. A description will be given of a screening test that can be safely done with a comparatively small amount of sample in a short period of time. First, experimental methods are described, and a description is then given of examples and results. It should be noted that the SADT test is excluded from this book because it is contained in the previous work.

3.2 DSC or DTA Using a Sealed Cell (A)

3.2.1 Test methods

A1. Names of the tests

Sealed cell – differential scanning calorimetry (SC–DSC) test and sealed cell – differential thermal analysis (SC–DTA) test

A2. Properties to be tested

The heat of decomposition and the extrapolated decomposition temperature of self–reactive substances are determined by DSC (or DTA), and fire and explosion hazards may be estimated from these parameters.

Table 3.1 The practical test methods evaluating fire · explosion hazards of reactive chemicals

Phenomena	Types of hazards			
	Possibility		Occurring frequency	
Detonation	SC-DSC	50/60 Steel tube 50/60(under sand)	Ignitability Friction	Drop ball Ballistic mortar Explosion underwater Electronic spark
Deflagration	Ignitability SC-DSC	50/60(underwater) Ballistic mortar Ballistic pendulum time/pressure Flash point	Drop ball	Ballistic mortar Ballistic pendulum Explosion underwater Ignitability Time/pressure
Thermal Explosion	SC-DSC PVT		SC-DSC PVT	SADT
Mixing ignition	SC-DSC	Mixing ignition Modified iron vessel	SC-DSC	Mixing ignition Modified iron vessel Small dewar

Phenomena	Types of hazards			
	Large or little		Violence	
Detonation	SC-DSC	Explosion underwater Ballistic mortar ballistic pendulum	Explosion under sand Drop ball	Explosion underwater
Deflagration	SC-DSC		Ignitability	Burning rate(IMO) Burning rate(UN, Fire Service Law Time/pressure
Thermal Explosion	SC-DSC	PVT		PVT
Mixing ignition	Small Dewar		Modified iron vessel	Mixing ignition

A3. Test apparatus

A3.1 DSC apparatus

Use a commercially available DSC or DTA apparatus.

A3.2 Sealed cell

Use, for example, the sealed stainless steel cell * shown in Figure 3.1.

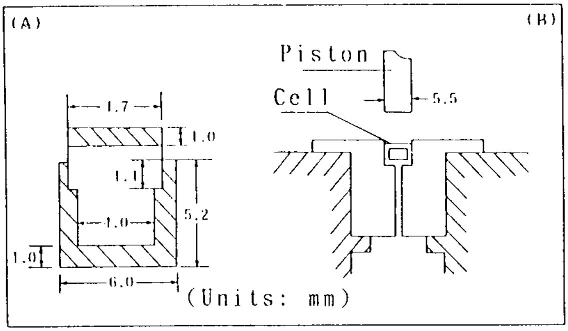

Fig. 3.1 Sealed Cell (A) and Hermetical Sealing (B)

* Leakless sealed cells and sealing device are now available from Seiko Instruments Inc. and Nippon Kayaku Co., Ltd.

A3.3 Measuring conditions

Measurements shall be made under the following conditions.

Heating rate : 10 ° C/min.
Maximum temperature : 550 ° C
Gas used : N_2, 40ml/min.
Amount of sample : 1−3mg
Standard samples : Tin, indium, potassium nitrate, and potassium perchlorate

A4. Test Procedures

Perform the following procedures for sample preparation and DSC operation. These procedures also apply to DTA operation.

(1) Weigh a sample cell and a lid.

(2) Place 1−3 mg of sample in the cell, determine the gross weight. Calculate the net weight by subtracting the tare from the gross weight.

(3) Cover the cell with the lid, and set it in the hole of a sealing device as illustrated in Figure 3.1(B).

(4) Hit the top of the cell and lid strongly with the pestle of the sealing device to seal it hermetically.

(5) Place the sealed sample cell on the cell holder on the sample side. Similarly seal an $\alpha-Al_2O_3$ containing cell, and place it on the cell holder on the reference side.

(6) Perform DSC at a heating rate of 10 °C/min.

(7) When a DSC curve is obtained, stop the measurement, and weigh each cell to verify that there is no leakage.

(8) Read the calorific value (Q_{DSC}) and the extrapolated decomposition onset temperature (T_{DSC}) from the curve.

The calorific value is proportional to the area under the DSC curve. This relationship is expressed by the equation:

$$M \cdot \triangle H = K \cdot A$$

where,

M :	mass (mg) of sample
△ H :	amount (mcal/mg) of energy change per unit mass of sample
K :	apparatus constant (mcal/mcal *)
A :	peak area (mcal *)

It should be noted that mcal * indicates the quantity of heat determined from the peak area on a recording chart.

The apparatus constant shall be determined as follows. First, prepare the melting curves for pure tin, indium, potassium nitrate, and potassium perchlorate. Next, using the value of heat of fusion found in the literature, determine the relationship between the temperature and the apparatus constant. Calculate the apparatus constant at the extrapolated decomposition temperature, and, in the abovementioned equation, use the value so obtained.

A5. Example of interpretation of test results

A5.1 Evaluation of the possibility of detonation or deflagration propagation

Plot values of the log of Q_{DSC} for a boundary detonating−substance (70% 2,4−dinitrotoluene) and a boundary deflagrating−substance (80% dibenzoylperoxide) against their respective values of log (T_{DSC} − 25), and draw a straight line passing through these data points. Using the same apparatus, determine the Q_{DSC} and T_{DSC} for the sample, and plot the data on the same graph. When the data point from the sample is located above the straight line,the sample is considered to have propagational qualities.

When a boundary propagational−substance is a mixture of a self−reactive substance and an inert substance in a pure form, the SC−DSC measurement is made on the pure self−reactive substance, and the value obtained by multiplying the value of Q_{DSC} by the ratio of the amount of the self−reactive substance to the boundary substance may also be used as the value of Q_{DSC} for the boundary substance.T_{DSC} is not changed by dilution.

A5.2 Estimation of SADT

The estimation of SADT is shown on page 201 of the previous book [1] .It should be noted, however, that the temperature of start of decomposition by DSC is not the extrapolated decomposition temperature but the temperature at which the curve begins to rise.

3.2.2 Test method stipulated in the Japanese Fire Services Law (A')

1. Thermal analysis test

(1) Objective

The purpose of this test is to evaluate the explosiveness of solid or liquid substances. For this purpose,measurements are made of the exothermic characteristics due to self-reactivity, such as the decomposition reaction induced in association with a rise in test article temperature.

(2) Standard substances

Use 2,4-dinitrotoluene (DNT) and dibenzoylperoxide (BPO) as the standard substances.

(3) Test Apparatus

Use a differential scanning colorimeter (DSC) or differential thermal analysis (DTA) apparatus [*1] with aluminium oxide (α – alumina) as the reference substance.

(4) Test Procedures

(a) Procedure for the standard substance

Set the hermetically sealed pressure cell [*2, *3] containing a standard substance (1mg of DNT or 2mg of BPO) on the test apparatus, and heat at a rate of 10 °C/min. Determine the exothermic start temperature and calorific value on the recording chart [*4]. Perform the test five times, and determine the average of the five runs.

(b) Procedure for the test article

Same as (a) above except that the amount of sample is about 2mg (but modified according to the calorific value).

(5) Interpretation

On a logarithmic scale, plot the calorific value against the value obtained by subtracting 25 °C from the exothermic start temperature. When the data point plotted is located on or above the straight line passing through the data points for DNT and BPO (calorific values are multiplied by 0.7 and 0.8,respectively),the sample is considered dangerous [*5].

---

*1 A high-pressure DTA or high-pressure DSC apparatus may be used.

*2 Use a cell made of the stainless steel that can withstand a pressure of about 5MPa.

*3 Pin-hole type cells cannot be used in DSC or DTA.

*4 Data on the recording chart shall be analyzed as follows:

(1) The line connecting the exothermic start point and end point is taken as the base line.
(2) The exothermic start temperature is determined from the intersection of the tangential line at the inflection point and the baseline.
(3) If any shoulder appears at the peak, consider the peak area in calorific value determination.
(4) If more than one peak appears, determine the exothermic start temperature from the first peak and calorific value by totaling the values from all peaks.

*5 When already producing heat at ordinary temperature, substances are considered hazardous materialswithout conducting the test.

(6) Example: Azodicarbonamide (ADCA)

(a) Morisaki's Data

Source :a) S. Morisaki and T. Ando, "DSC Data Book on Reactive Substances", Safety data of the Research Institute of Industrial Safety, RIIS−SD−87, No.1 (1987)

b) S. Morisaki, et al., "Development and Research of a Danger Prediction System for Reactive Substances", Futurological Engineering Institute (1986)

DSC : Product of Du Pont Co., thermal−flux type

Atmosphere : argon

Pressure : 34 kg/cm^2

Amount of sample : 1−2mg

Temperature rise rate : 10 ° C/min.

Sample container : aluminium, pin−hole cell

Table 3.2 Pressure DSC Data on Standard Substances and ADCA (Source: from Morisaki)

Substances	Atmosphere	No. of samples	T_{DSC} (°C)	Q_{DSC} (cal/g).......	log(T_{DSC}−25)	logQ_{DSC}
100% 2,4−DNT [a]	Argon	1	312	829	2.46	2.92
70% 2,4−DNT	−−	−	312	580	2.46	2.76
100% BPO [a]	Argon	1	106	438	1.91	2.64
80% BPO	−−	−	106	350	1.91	2.54
100% ADCA [a]	Argon	1	209	156	2.26	2.19
100% ADCA [b]	Argon	−	205	368	2.2	2.56

3.2.3 Results

To our knowledge, data have been obtained by four study groups.

DSC(1) data were obtained with a Model DSC20 apparatus (Shimadzu Co., Ltd.) at Yoshida laboratory, The University of Tokyo. A sealed cell made of soft stainless steel was used as the sample cell [8, 9]. The extrapolated decomposition temperature [10] was taken as the decomposition start temperature (T_{DSC} or T_{DTA}). In DSC(1),the peak area was obtained by weighing the peak−area cutout. The apparatus constant, k, which is used to determine the DSC decomposition heat ($Q_{DSC}(1)$) from the peak area, was determined by obtaining the values of heat of fusion for potassium nitrate, indium, tin, and potassium perchlorate.

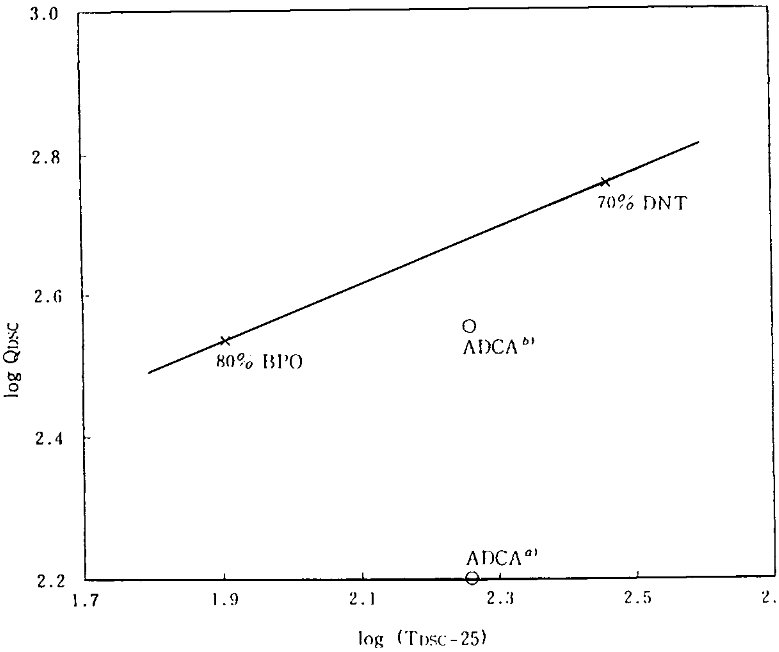

Fig. 3.2 The plot of log(T_{DSC}−25) vs. logQ_{DSC}

DTA(2) data were obtained with a Model DT−40 DTA apparatus (Shimadzu Co., Ltd.) at Yoshida laboratory. Since the DSC apparatus developed problems frequently, an attempt was made to use a DTA apparatus in screening tests for the hazards of reactive substances. The sample cell used was the same as in DSC(1). Q_{DTA}(2) was determined by using the apparatus constant, k, at each temperature as obtained in the DTA evaluation of the standard substances listed above. The DTA curve was stored on a floppy disk by a Model PC−9801 personal computer (NEC), and the values of T_{DTA} and peak area were determined with the base line leveled. The peak area was calculated as the product of output voltages (μ V) times temperature (° C) and, by multiplying the resulting peak area by the apparatus constant, Q_{DTA}(2) was determined.

DSC(3) data were obtained with a Model DSC−200 apparatus (Seiko Instruments Inc.) at the Koriyama Plant of Nippon Peroxide Co., Ltd. The sample cell used was a sealed cell supplied from Seiko Instruments Inc. T_{DSC}(3) and Q_{DSC}(3) were determined directly by the processor supplied with a DSC apparatus.

DSC(4) data were obtained with a Model DSC−910 DSC apparatus (Du Pont) at Morisaki's laboratory, Research Institute of Industrial Safety [11] . This apparatus was a thermal−flux type pressure DSC apparatus. Data were obtained in argon atmosphere at 3.5MPa. The sample cell used was a pin−hole aluminum cell. Data was processed by the processor supplied with the DSC apparatus.

These experiments were all carried out with several mg of sample at a heating rate of

10 ° C/min.

In the original Japanese version of this book, there are Figures 3.3 and 3.4, and Tables 3.3, 3.4 and 3.5, which are omitted in this English version. These original Figures and Tables are diffuse and lengthy. Especially regarding to Table 3.5, the readers of this book are adviced to refer to newer literatures. We defined the EP function, which is expressed as follows:

$$EP = \log Q_{DSC} - 0.38 < \log (T_{DSC} - 25) - 1.72$$

EP is a function for the estimation of propagational quality. When the EP is "+", the sample is judged to have propagational qualities.

3.2.4 Experience with SC–DSC at Yoshida laboratory

At Nanba laboratory, Professor Nanba was the predecessor of Professor Yoshida. A DSC apparatus was purchased with a Government subsidy for aiding scientific research in the early 1970's. To determine the thermal decomposition characteristics of unstable substances, the literature was surveyed[14)] in collaboration with S.Takeyama (Kinki University), then a student in the master's course of The University of Tokyo. As a result, DSC was found to be of very wide application. Moreover, a preliminary experiment showed that sealed cells were necessary for studying the decomposition reaction of self–reactive substances. For most self–reactive substances, evaporation or sublimation may occur before exothermic decomposition during DSC measurement made in an open cell at room temperature. This makes it impossible to measure an accurate heat of decomposition.

Sealed cells were made on an experimental basis by K.Okawa (Okawa Seiki Co., Ltd.)[15)]; the first was made of aluminium. Experiments with this cell showed that an interfering peak appeared and no clear–cut peaks due to the decomposition of a sample could be obtained. Next, a sealed cell was made of soft stainless steel. Clear–cut peaks could be obtained by the use of this cell. At this time, the pressure–proof property of the cell was found to be 4.5 ± 1 MPa as determined from the temperature at which, when filled with water and then heated, it blew up.

Professor Uetake at Nippon University presented an interesting report of an experiment on the necessity of using a sealed cell. In this experiment, pinholes of different diameters were made in lids of cells without achieving completely hermetical sealing and DSC measurements were made on organic peroxides. It was reported that satisfactory results could be obtained even when the cell was not completely hermetically sealed. In our experience, however, the determined value of Q_{DSC} is frequently low when sample leakage occurs from a cell. On the basis of this finding, we recommend the use of completely hermetically sealed cells in evaluating the explosion danger of unspecified substances.

A study of the kinetics of thermal decomposition reactions using pentaerythritol tetranitrate(PETN), a high explosive, as the model substance was first conducted by SC−DSC. In this study, information was obtained that was relative to the characteristics of the DSC technique. However, the question as to how the results of analyses of this type were useful for practical work arose, and studies in this area were stopped. Subsequently, studies have proceeded on the evaluation of hazards by collecting as much data on self−reactive substances as possible.

In the beginning, the authors made SC−DSC measurements on combination explosives 8). The report on these measurements was translated into English at the U.S. Department of Energy. We have been consulted by several companies with respect to the evaluation of hazards of self−reactive substances. In these instances, we have inevitably referred to SC−DSC data.

There are several problems concerning SC−DSC. One is the leakage frequently encountered in sealed cells. We make it a rule to accurately weigh the sample after filling a sealed cell and after the DSC measurement. In this situation, the weight may be decreased occasionally after the measurement. We have gotten around this problem by improving the sealing technique and the sealing device. Recently, satisfactorily sealed cells have been introduced by Seiko Instruments Inc. and Nippon Kayaku Co., Ltd.

In 1981, Yoshida called at the safety laboratories of chemical companies in Switzerland and West Germany, taking advantage of the opportunity of attending the OECD − IGUS (the Organization for Economic Cooperation and Development − International Group of Experts on the Explosion Risks of Unstable Substances). In the laboratories visited, SC−DSC is used. Dr.Berthold at BASF AG. said that newly synthesized substances were all analyzed by SC−DSC and that DSC data on as many as 8,000 substances were kept in custody at BASF. This company was considerably different in the amount of data collected when compared to chemical companies in Japan at that time. At present, however, SC−DSC is used in Japan to evaluate the danger of newly synthesized compounds, as in Fuji Photo Film Co., Ltd.

Sealed cells similar to our cells in operation were used at Ciba−Geigy AG, and screwed−type sealed cells at BASF. Screwed type sealed cells with a bursting plate are available from Metlar Co., an instrument manufacturer in Switzerland.

Another problem is the ease with which a DSC apparatus degrades. Briefly, after it is used for a long time, it begins to produce noise, such that no definite DSC curve can be obtained. This may be attributable to the contamination of cell holders by gas from samples. The authors have conducted experiments with sealed cells by passing nitrogen gas through them, but contamination and its related noise production could not be avoided. For a time, a DTA apparatus considered less prone to contamination was borrowed from Nippon Kayaku Co., Ltd. and used for investigative purposes.

In the case of DTA, the apparatus constant varies with the temperature; therefore, the constant must be determined at several temperatures to measure Q_{DTA}. Although a theory that Q_{DTA} shows wider variations than Q_{DSC} has been published, whether this causes any problem in the evaluation of hazards is now under consideration. To solve the problems of gas leakage and the expense of the cells, screwed type sealed cells were evaluated by W.Lin 17), a student sent from Chung Shang Institute of Science and Technology (Taiwan, R.O.C.) to Japan. Although expensive, screwed type sealed cells have an advantage in that they are free from leakage and can be used repeatedly. On the other hand, however, the large mass of a screwed type sealed cell may cause the base line to drift. In addition, washing the cells for reuse is a troublesome job. For these reasons, sealed cells of this type were discontinued.

Several attempts have been made to improve driven type sealed cells, as shown in Figure 3.5.

The cell shown in Figure 3.5(a) is the first attempt at an improved sealed cell. Its lid is tailored to fit the cell, placed in the correct position on the cell, and then held in place by crimping the brim. The cell shown in Figure 3.5(b) is designed with the matching surfaces of the cell and lid tapered to prevent leakage. The cell presented in Figure 3.5(c) is designed to prevent leaks and to resist pressure by having the top of the cell held down from the outside. Although satisfactory results were obtained from these cells to some extent, leakage increased after a time. The probable reason for this is that the repeated use of a sealing device causes misalignment of its shaft or deformation of its pestle; hence, the sealing device itself must be properly maintained to ensure optimum performance.

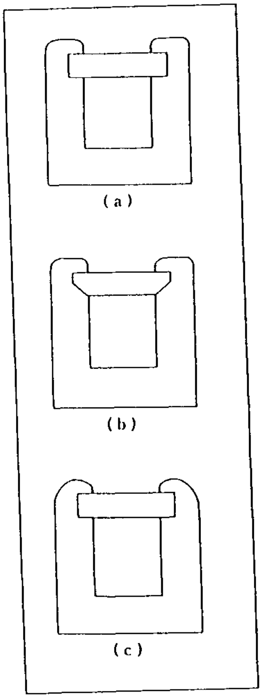

Fig. 3.5 Improved Driven−Type Sealed Cell

The next matters for consideration are the effects of pressure. In a sealed cell, pressure increases as the sample decomposes. While the increase in pressure prevents evaporation of the sample,the pressure change may influence the rate of reaction and heat of decomposition.

Morisaki at the Research Institute of Industrial Safety has made a number of DSC measurements as a function of pressure 18, 19) and determined the effects. According to his findings, the Q_{DSC} values for some substances are influenced by pressure, while those for others are not. When substances for which Q_{DSC} values are influenced by pressure are subjected to DSC measurement in sealed cells, the pressure will depend on the amount of sample used and, therefore, the values of Q_{DSC} will inevitably vary. We will neglect this factor for the present.

Important parameters to be determined by SC–DSC are the extrapolated decomposition temperature (T_{DSC}) and heat of decomposition (Q_{DSC}). Of these parameters, the values of T_{DSC} did not vary when measured in four kinds of SC–DSC, SC–DTA, and pressure–DSC apparatuses 13) . Furthermore, since slight errors in T_{DSC} do not influence the estimation of explosiveness, T_{DSC} and T_{DTA} are considered less significant. For Q_{DSC}, on the other hand, it has been found that errors in its determination have a considerable effect on the evaluation of explosive potential and that its values show great variation and apparatus dependent deviations. The cause of these may be attributed in part to leakage from a sealed cell. In addition, Q_{DSC} may vary depending on the manner of measuring the exothermic–peak area. From our own experience we know that, as seen in Figure 3.6, exothermic–peak area varies with the manner of measurement. In Figure 3.6(a), (b) and (c) show the peaks of tetryl (a high explosive), trinitrotoluene (TNT; a high explosive), and dinitrosopentamethylenetetramine (DPT; a blowing agent), respectively. The peak area depends largely on the level at which the base line is established. In the case of tetryl, the area both in (a1) and (a2) is incorrect; the correct peak area is intermediate between that in (a1) and (a2). In this instance, the heating rate should be decreased to separate the two peaks from each other as far as possible. For TNT, (b2) shows the correct area. Much information is available concerning the value of Q_{DSC} for DPT. The Q_{DSC} value reported varies. For the present, it is difficult to determine whether (c1) or (c2) is correct.

The pressure–proof capability of a sealed cell has limitations, and the pressure generated in a sealed cell depends on the amount of gas produced by the substance being tested. The amount of sample for typical self–reactive substances is thus confined to 1 to 3 mg. This is an advantage of the SC–DSC method in that safety is ensured and that a trace amount of sample suffices. In contrast, the difficulty of accurately weighing a sample and the occurrence of relative errors are problems. Moreover, no correct exothermic peaks may be obtained if the amount of sample is too small. For these reasons, a suitable amount of sample is considered from 1 to 3 mg.

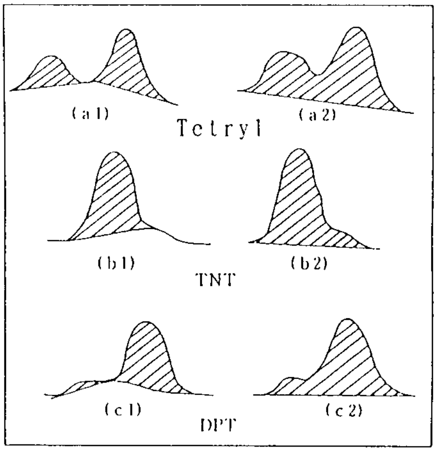

Fig. 3.6 Peak Shapes and Areas

3.2.5 Desirable method for the prediction of explosive potential by SC-DSC (or SC-DTA)

As has been discussed, several requirements must be met to predict the explosiveness of self-reactive substances on the basis of the results of measurements by SC-DSC. First, a leak-free sealed cell must be used that is sufficient pressure-proof. Such cells are available from Nippon Kayaku Co. and Seiko Instruments Inc. Next, correct peak areas must be measured. Determination of correct exothermic peaks is one requisite for this purpose, and it is necessary to acquire some experience in this task.

Another requisite is to measure the areas of peaks accurately. In our office, areas of exothermic peaks on DSC charts have been determined for many years by weighing their cutouts. At one time,an attempt was made to use a planimeter, but this method was not used long. In recent years personal computers have come into wide use. The authors have also connected the DSC apparatus directly to a computer which collects and analyzes the data and prints out the results. This system marks a great advance in that peak areas can be measured accurately.

In order to determine the presence of propagational qualities without any deviation, it may be desirable to use a sealed cell filled with a known amount of boundary propagational substance. Furthermore, a reference cell which is filled with a substance of known calorific (endothermic) value is also useful for accurately measuring the heat of decomposition. In order to obtain clear-cut exothermic peaks over a distinct base line, the heat capacity of the sample cell must be the same as the reference cell; therefore, a sample cell of as close to equivalent mass as possible must be used. Moreover, reference cells of different masses need to be kept on hand so that the mass of a sample-containing cell may be matched with that of an available reference cell.

An SD-DSC test is highly useful for screening the danger of explosion of self-reactive substances. When the result of an SD-DSC test lies in the border zone between the explosive and nonexplosive regions, however, a more reliable standard propagational test should be conducted to determine which quality is accurate.

3.3 Impact Sensitivity Tests

3.3.1 General drop ball type impact sensitivity test (B)

B1. The name of the test

Drop ball impact sensitivity test

B2. The properties to be tested

Ease with which ignition or explosion occurs upon impact for relatively sensitive self-reactive substances.

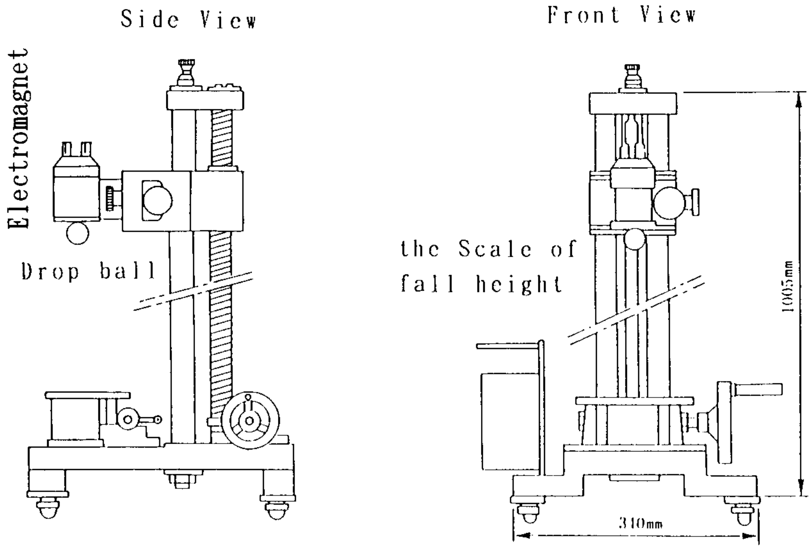

Figure 3.7 The small sized drop ball test equipment

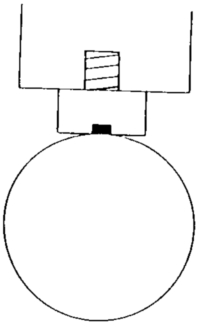

Figure 3.8 The adaptor for
small sized ball

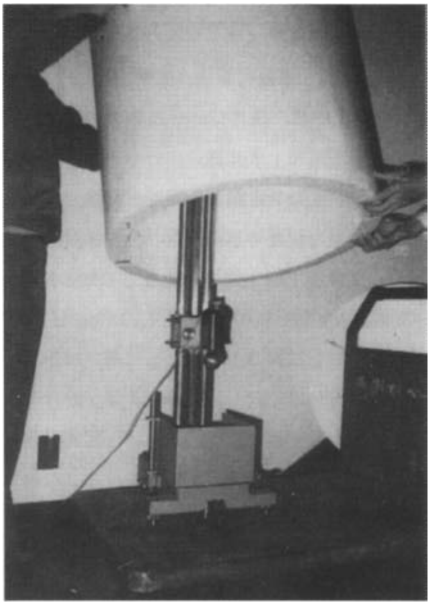

Figure 3.9 The muffler pipe for
reducing the noise [20)]

B3. Test equipment

B3.1 Drop ball test equipment

Two different kinds of equipment were used by the authors. Both were manufactured by Kuramochi Kagakukikai Co., Ltd.

(1) Small-sized drop ball test equipment

Figure 3.7 shows the front and side views of the test equipment. To hold balls of varying diameter in the center of an electromagnet, a screw hall with a 5mm diameter and 25mm depth is located in the center at the lowest end of the electromagnet. The adapter shown in Figure 3.8 can be attached to hold small drop balls in the center of the electromagnet. The ball is released when the electric current is turned off. For this purpose this equipment has a rectifier with a switch for turning the electromagnet on and off. Small drop balls are occasionally magnetized by the electromagnet. When this happens, the magnetic strength of the electromagnet should be reduced. Samples are put on steel rollers 12mm high and 12mm in diameter in the direct impact method or in between the rollers for the indirect method.

Other tools to be used are as follows.

1) Desiccator for drying the oxidizer.
2) Desiccator for drying the red phosphorus.
3) Microspatula for use with the oxidizer only.
4) Microspatula for use with red phosphorus only.
5) Agate mortar and pestle for pulverizing the oxidizer.
6) Tissue papers for cleaning.
7) Water filled plastic vessel for temporary storage of used rollers.
8) Water filled plastic vessel for temporary storage of used tissue papers.
9) Sandpaper for polishing the surface of the rollers.
10) Earmuffs.
11) Muffler pipe for samples producing loud noises (like sporting paper cap, PETN, RDX, HMX, and primary explosives) shown in Figure 3.9.

(2) Large-sized drop ball test equipment

This equipment is modified from the 5kg drop hammer test equipment called for by Japanese Industrial Standards (JIS). A 5kg drop hammer was removed from the original equipment which was modified to attach 2kg and 5kg steel ball bearings. The front view of this equipment is shown in Figure 3.10.

(3) Drop balls

Steel balls 1g to 5kg in weight are used.

B4. Test procedure

To avoid any danger to the operators, sample weights should be limited to a total mass of 10mg. When the tests for highly sensitive systems like oxidizers with red phosphorus are carried out, those substances should placed on the sample steel roller.

As the samples which explode in this test are highly sensitive substances, one can judge "go" (meaning an explosion occurred) or "no go" (no reaction) with sufficient accuracy by this simple test. In the case of primary explosives, wet primary explosives should be put on the steel roller and should be dried in a desiccator.

(Fig. 3.10 and Fig. 3.11)

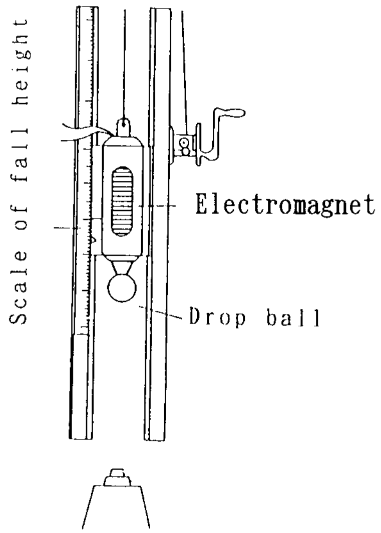

Fig. 3.10 The large sized drop ball test equipment

B4.1 The up and down method

B4.1.1 Direct impact method

(1) 4–10mg of sample powder are put on the upper surface of a steel roller 12mm high and 12mm in diameter.

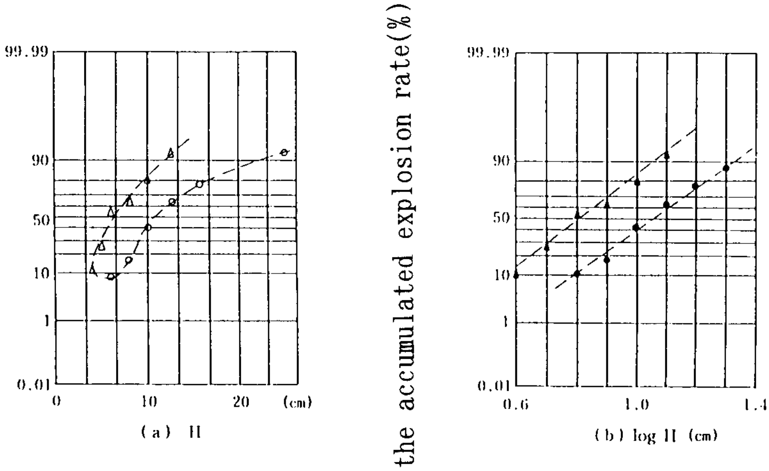

Figure 3.11 The accumulated explosion rate plotted on semi–log paper in normal and logarithm scale with Sporting Paper Cap.

▲△ : direct impact using 36g of ball

●○ : indirect impact using 397 g of ball

(2) The steel roller with the sample powder is placed in the center of the anvil on the drop ball test equipment.

(3) A ball of adequate weight is selected and attached to the equipment.

(4) The distance (fall height H(cm)) between the lower end of the ball and the upper surface of steel roller should be selected in the following manner: H should be at some interval with $\Delta \log H = 0.1$ as the standard height of $\log H = 1.0$.

(5) After the ball is dropped, a judgment for "go" (sound, fire or smoke observed) or "no go" (no reaction noted) should be made.

(6) After many trials, the critical heights at which the sample response changes from "go" to "no go" or the reverse is determined.

(7) When these critical heights are found, tests should be done one step higher and one step lower. After that the fall height should be lowered when sample response is "go" and should be raised when it is "no go". Tests should be continued following this procedure.

(8) In total 20 tests, including 2 tests of the critical height, should be done.

(9) The substances whose response showed "no go" at $\log H = 1.8$ ($H = 63.1$ cm) with a 535g steel ball should be tested six times at this height and the number of times "go" is noted should be recorded.

When the system of an oxidizer and flammable substances (e.g. red phosphorus) is tested, procedure (1) above should be changed in the following fashion.

(1')Approximately 2−6mg of red phosphorus are rubbed on a steel roller 12mm in diameter and 12mm high with a microspatula. Approximately 2−6mg of oxidizer are loaded carefully on the red phosphorus. Samples of oxidizer that are plastic should be pressed carefully on red phosphorus. The sample weights are selected at the values mentioned above because there is no danger of accidental explosion and clear judgment may be made based on an explosive sound or fire when the sample is ignited upon impact.

B4.1.2 Indirect impact method

The indirect impact method should be used when the data generated from the direct impact test method is widely spread. The test procedure for this method only differs from the direct impact method in part (2) as described in the following 20).

(2') A steel roller of the same size is placed on the steel roller with the sample. They should be positioned in the center of the anvil on the test equipment after the sample has been distributed uniformly between the rollers.

B4.1.3 Data treatment

After data are collected via the up and down method 21), the 50% explosion height (H_{50},cm) is determined and the energy (E_{50},J) of ball dropped at 50% of the explosion height is calculated. Test results should be recorded as in the example in Table 3.6.

Table 3.6 Example of test results of drop ball test

Trials number	sample	$KClO_4$ - P	$KClO_4$ - P	$Pb(N_3)_2$	$Pb(N_3)_2$	black powder	black powder
	weight of ball (Kg)	0.005	0.005	0.173	0.173	4.26	4.26
	impact method	direct	indirect	indirect	direct	indirect	direct
1		Y(0.8)	Y(1.2)	Y(1.4)	Y(1.0)	Y(1.5)	Y(0.7)
2		N(0.7)	N(1.1)	N(1.3)	N(0.9)	N(1.4)	N(0.6)
3		Y(0.8)	N(1.2)	N(1.4)	Y(1.0)	N(1.5)	Y(0.7)
4		N(0.7)	Y(1.3)	N(1.5)	N(0.9)	Y(1.6)	Y(0.6)
5		Y(0.8)	N(1.2)	Y(1.6)	Y(1.0)	N(1.5)	N(0.5)
6	Y:"go"	Y(0.7)	Y(1.3)	N(1.5)	Y(0.9)	N(1.6)	N(0.6)
7	N:"no go"	N(0.6)	Y(1.2)	Y(1.6)	N(0.8)	Y(1.7)	Y(0.7)
8		N(0.7)	N(1.1)	N(1.5)	Y(0.9)	N(1.6)	N(0.6)
9	value	N(0.8)	Y(1.2)	N(1.6)	Y(0.8)	Y(1.7)	Y(0.7)
10	:log H	Y(0.9)	N(1.1)	N(1.7)	Y(0.7)	N(1.6)	Y(0.6)
11		N(0.8)	N(1.2)	Y(1.8)	Y(0.6)	N(1.7)	Y(0.5)
12		Y(0.9)	Y(1.3)	N(1.7)	Y(0.5)	Y(1.8)	Y(0.4)
13		N(0.8)	N(1.2)	Y(1.8)	N(0.4)	N(1.7)	N(0.3)
14		N(0.9)	Y(1.3)	N(1.7)	N(0.5)	Y(1.8)	N(0.4)
15		Y(1.0)	N(1.2)	Y(1.8)	N(0.6)	N(1.7)	Y(0.5)
16		Y(0.9)	Y(1.3)	N(1.7)	N(0.7)	Y(1.8)	N(0.4)
17		Y(0.8)	N(1.2)	Y(1.8)	N(0.8)	Y(1.7)	N(0.5)
18		N(0.7)	N(1.3)	Y(1.7)	Y(0.9)	N(1.6)	N(0.6)
19		N(0.8)	Y(1.4)	Y(1.6)	N(0.8)	Y(1.7)	Y(0.7)
20		Y(0.9)	N(1.3)	N(1.5)	Y(0.9)	Y(1.6)	Y(0.6)
$\log H_{50}$		0.8	1.23	1.62	0.76	1.64	0.55
$\log E_{50}$		−2.51	−2.08	−0.14	−1.00	1.26	0.17
standard deviation (σ) of $\log H_{50}$		0.11	0.07	0.28	0.45	0.15	0.19

Table 3.7 Data sheet for calculation

logarithm drop height(log H)	"go" counts(n)	i	i×n	i2×n
0.3	0	0	0	0
0.4	1	1	1	1
0.5	1	2	2	4
0.6	4	3	12	36
0.7	3	4	12	52
	Ns=9		A=27	B=93

The data treatment for the up and down method is as follows, using the example of data from table 3.6.

(1) A table of collected data (Table 3.7) is prepared. Fall heights are put in the first column, arranged lowest to highest. In the third column i is the increase in step number from the lowest fall height.

(2) The 50% explosion height (H_{50} ,cm) is calculated using following equation,

$$\log H_{50} = C + d\,(A/Ns \pm 1/2)$$

where n = the number of "go" or "no go" entries (small number of total sample should be used), $Ns = \Sigma n$, $A = \Sigma (i \times n)$, C = common logarithm of the lowest fall height (i = 0), d = fall height interval of log H, $\pm = -$ should be selected when the number of "go" entries is used, + should be selected when the number of "no go" entries is used.

(3) The standard deviation (S) of log H is calculated with following equation,

$$S = 1.62d\,\{(Ns \cdot B - A^2)/Ns^2 + 0.029\}$$

where B means $\Sigma (i^2 \times n)$.

(4) The 50% explosion energy (E_{50} ,J) corresponding to the 50% explosion height (H_{50} ,cm) is calculated with following equation.

$$E_{50} = 0.098 \times M \times H_{50}$$

where M is the drop ball weight in kg.

B4.2 Tests at fixed height

At the 50% explosion height determined via the up and down method, the results are repeated 10 times or 40 times and the sensitivity of the sample is estimated with 0/10, 10/10 or 20/40.

3.3.2 Example of test results

Examples of test result run in the author's laboratory are shown in Table 3.8.

3.3.3 Properties of the drop ball impact sensitivity test

3.3.3.1 1/6 explosion height and 50% explosion height [21, 24] .

Some errors are unavoidable in impact sensitivity tests like the drop hammer test and drop ball test. Important questions involve the precision and accuracy of acquired results. During the World War II in U.S.A., statistical investigations on drop hammer tests were carried out mainly by Professor Dixon [21] at the Bruceton Laboratory to achieve greater accuracy in determining impact sensitivity with the fewest trials.

As the result of these investigations, the 50% explosion height determination method using the up and down technique was confirmed as a superior test method. It requires the fewest trials, it yields highly reliable results, and it is accurate. The 50% explosion

Table 3.8 The results of drop ball test
(Indirect impact method and direct impact method)

		Indirect impact method			Direct impact method		
		log E_{50}	σ of log H_{50}	ref. No.	log E_{50}	σ of log H_{50}	ref. No.
Mixture of Oxidizer / Combustible substance							
Chlorites	$NaClO_2$/P	-2.12	0.13	[3]	-2.85	0.08	[2]
	bleaching powder/P				>0.42		[2]
Chlorates	$AgClO_3$/P	-2.77	0.093	[1]	-3.50	0.08	[2]
	$AgClO_3$/S	-2.39	0.035	[1]			
	$AgClO_3$/Mg	>0.30		[1]			
	$Ba(ClO_3)_2$/P				-2.25	0.31	[2]
	$KClO_3$/P	-2.08	0.07	[1]	-2.50	0.08	[2]
		-2.39	0.19	[10]	-2.51	0.11	[2]
		-2.80	0.12	[10]			
		-3.11	0.10	[10]			
		-2.95	0.10	[10]			
		-2.41	0.22	[9]			
		-2.75	0.17	[9]			
		-2.73	0.26	[9]			
		-2.48	0.26	[9]			
		-2.56	0.37	[9]			
		-2.89	0.73	[10]			
		-2.55	0.43	[10]			
		-2.69	0.53	[10]			
		-2.72	0.15	[10]			
		-3.06	0.19	[10]			
		-2.43	0.33	[10]			
		-2.50	0.21	[10]			
		-2.57	0.09	[10]			
		-2.57	0.13	[10]			
		-2.54	0.23	[10]			
		-2.27	0.19	[10]			
	$KClO_3$/S	0.07	0.19	[1]	-0.97	0.08	[9]
					-0.90	0.15	[9]
					-0.85	0.06	[9]
					-1.00	0.09	[9]
					-0.89	0.08	[9]
					-0.89	0.07	[9]

Table 3.8 The results of drop ball test (continued)
(Indirect impact method and direct impact method)

		Indirect impact method			Direct impact method		
		log E_{50}	σ of log H_{50}	ref. No.	log E_{50}	σ of log H_{50}	ref. No.
mixture of Oxidizer / Flammable substance							
	$KClO_3/EG^{a)}$	-0.15	0.24	[1]			
	$KClO_3/As_4S_4{}^{a)}$	-0.59	0.32	[1]			
	$KClO_3/Al$	>0.30		[1]			
	$KClO_3/Mg$	>0.30		[1]			
	$KClO_3/CEL^{a)}$				-0.50	0.07	[9]
					-0.72	0.25	[9]
	$NaClO_3/P$	-2.32	0.045	[1]	-3.17	0.16	[2]
Chlorates	$NaClO_3/S$	-0.63	0.103	[1]			
	$NaClO_3/EG^{a)}$	-0.35	0.104	[1]			
	$NaClO_3/Al$	>0.30		[1]			
	$NaClO_3/Mg$	>0.30		[1]			
	$KBrO_3/P$	-1.80	0.45	[2]	-2.84	0.07	[2]
	$NaBrO_3/P$	-1.29	0.14	[1]	-2.54	0.36	[2]
	$NaBrO_3/S$	0.14	0.07	[1]			
Iodates	$AgIO_3/P$				-0.88	0.16	[2]
	$Ba(IO_3)_2/P$	0.35	0.13		-0.25	0.03	[2]
	HIO_3/P	-0.90	0.057	[2]	-1.42	0.06	[2]
	HIO_3/S	>0.30		[1]			
	$HIO_3/EG^{a)}$	>0.30		[1]			
	KIO_3/P				-0.97	0.22	[2]
	NH_4IO_3/P	-0.46		[1]$^{b)}$	-0.33	0.15	[2]
	$NaIO_3/P$	0.09		[1]$^{b)}$	-0.31	0.23	[2]
Perchlorates							
	$Ba(ClO_4)_2 \cdot 3H_2O/P$	-0.77		[1]$^{b)}$	-1.08	0.08	[2]
	$Co(ClO_4)_2 \cdot 3H_2O/P$	-0.77		[1]$^{b)}$	-1.00	0.06	[2]
	$Fe(ClO_4)_2 \cdot 6H_2O/P$	-0.85		[1]$^{b)}$	-0.93	0.06	[2]
	$KClO_4/P$	-0.61	0.063	[1]	-0.70	0.04	[2]
	$KClO_4/EG^{a)}$	-0.14	0.105	[1]			
	$KClO_4/As_4S_4{}^{a)}$	>0.30		[1]			
	$KClO_4/Al$	>0.30		[1]			
	$LiClO_4/P$	-0.64		[1]$^{b)}$	-0.93	0.10	[2]
	$Mg(ClO_4)_2/P$	>0.30		[1]	-0.58	0.34	[2]

Table 3.8 The results of drop ball test (continued)
(Indirect impact method and direct impact method)

		Indirect impact method			Direct impact method		
		log E_{50}	σ of log H_{50}	ref. No.	log E_{50}	σ of log H_{50}	ref. No.
mixture of Oxidizer / Flammable substance							
	$NaClO_4$/P	-0.67	0.44	[1]	-1.0	0.12	[2]
	$NaClO_4$/S	0.37	0.07	[1]			
	$NaClO_4$/EG[a)]	0.28	0.18	[1]			
	NH_4ClO_4/P	-0.20	0.21	[1]	-1.0	0.08	[2]
	NH_4ClO_4/S	>0.30		[1]			
	NH_4ClO_4/EG[a)]	0.31	0.04	[1]			
	NH_4ClO_4/As_4S_4[a)]	>0.30		[1]			
	NH_4ClO_4/Al	>0.30		[1]			
	$RbClO_4$/P	-0.44		[1][b)]			
Periodates	KIO_4/P				-0.85	0.14	[2]
Nitrites	$AgNO_2$/P				>0.42		[2]
	KNO_2/P				>0.42		[2]
	$NaNO_2$/P	-0.04		[1][b)]	-0.62	0.09	[2]
Nitrates	$AgNO_3$/P	-0.48	0.12	[1]	-0.45	0.16	[2]
Nitrates							
	$Al(NO_3)_3 \cdot 9H_2O$/P	>0.30		[1]	>0.42		[2]
	$Ba(NO_3)_2$/P	0.10		[1][b)]	-0.23	0.13	[2]
	$Bi(NO_3)_3 \cdot 5H_2O$/P	-0.26		[1][b)]	0.18	0.53	[2]
	$Ca(NO_3)_2 \cdot 4H_2O$/P	0.11		[1][b)]	-0.47		[2]
	$Ca(NO_3)_2 \cdot 4H_2O$/P	>0.30		[1]			
	$Co(NO_3)_2 \cdot 6H_2O$/P	>0.30		[1]	>0.42		[2]
	$Cd(NO_3)_2 \cdot 4H_2O$/P				>0.42		[2]
	$CsNO_3$/P	-0.06		[1][b)]	-0.64		[2]
	$Fe(NO_3)_2 \cdot 6H_2O$/P	>0.30		[1]	>0.42		[2]
	$HgNO_3 \cdot H_2O$/P	0.20		[1][b)]	-0.64		[2]
	$Hg(NO_3)_2 \cdot 0.5H_2O$/P	-0.74		[1][b)]	-1.32	0.14	[2]
	KNO_3/P	0.11	0.14	[1]	-0.14	0.09	[2]
		0.20	0.18	[7,8]	-0.25	0.15	[c)]
		1.00	0.13	[7,8]	-0.65	0.04	[c)]
					-0.40	0.15	[c)]
					-0.59	0.18	[7,8]
					-0.49	0.05	[7,8]
					-0.62	0.14	[7,8]

Table 3.8 The results of drop ball test (continued)
(Indirect impact method and direct impact method)

	Indirect impact method			Direct impact method		
	log E_{50}	σ of log H_{50}	ref. No.	log E_{50}	σ of log H_{50}	ref. No.
mixture of Oxidizer / Flammable substance						
				-0.67	0.10	[7,8]
				-0.59	0.28	[7,8]
				-0.51	0.10	[7,8]
				-0.25	0.15	[7,8]
				-1.00	0.08	[10]
				-0.86	0.07	[10]
				-0.89	0.54	[10]
				-0.84	0.17	[10]
				-0.83	0.08	[10]
KNO_3/EG[a]	>0.30		[1]			
KNO_3/Al	>0.30		[1]			
$Ni(NO_3)_2\cdot 6H_2O$/P	>0.30		[1]	>0.42		[2]
$Mg(NO_3)_2\cdot 6H_2O$/P	>0.30		[1]	>0.42		[2]
$LiNO_3$/P	0.17		[1]	-0.45	0.25	[2]
NH_4NO_3/P	0.084	0.26	[1]	-0.15	0.06	[2]
NH_4NO_3/EG[a]	>0.30		[1]			
NH_4NO_3/Al	>0.30		[1]			
$NaNO_3$/P	-0.05	0.14	[1]	-0.25	0.22	[2]
$Sr(NO_3)_2$/P	0.06		[1][b]	-0.25	0.06	[2]
$Pb(NO_3)_2$/P	-0.11		[1][b]	-0.42	0.16	[2]
$Zn(NO_3)_2\cdot 6H_2O$/P	>0.30		[1]	>0.42		[2]
Dichromates $Ag_2Cr_2O_7$/P	0.12		[1][b]	-0.21	0.48	[2]
$K_2Cr_2O_7$/P				0.10	0.10	[2]
$Na_2Cr_2O_7\cdot 2H_2O$/P				>0.42		[2]
$(NH_4)_2Cr_2O_7$/P	0.27		[1][b]	0.30	0.30	[2]
Chromates Ag_2CrO_4/P	>0.30		[1]	0.32	0.08	[2]
$CoCrO_4$/P	>0.30		[1]	0.24	0.04	[2]
Peroxides BaO_2/P				-0.35	0.07	[2]
KO_2/P				-1.70	0.32	[2]
Na_2O_2/P	-2.04	0.32	[1]	-2.70	0.32	[2]
Na_2O_2/Al	>0.30		[1]			
CaO_2/P	>0.30		[1]	-0.12	0.20	[2]

MgO_2/P	>0.30		[1]	-0.08	0.12	[2]
SrO_2/P	>0.30		[1]	-0.06	0.24	[2]
ZnO_2/P	>0.30		[1]	-0.49	0.08	[2]
ZnO_2/EG[a]	>0.30		[1]			
ZnO_2/S	>0.30		[1]			
Explosives						
Octogen (HMX)	0.39	0.14	[3,5]	-0.47	0.12	[3,5]
Hexogen (RDX)	0.20	0.26	[3,5]	-0.44	0.09	[3,5]
	0.53	0.12	[4,5]	-0.02	0.24	[4,5]
Tetryl	0.13	0.15	[3,5]	0.03	0.37	[3,5]
	0.56	0.09	[4,5]	>1.5		[4,5]
Lead azide	-0.14	0.28	[3,5]	-1.00	0.45	[3,5]
				-0.03	0.08	[4,5]
DDNP[a]	-0.03	0.15	[3,5]	-0.86	0.19	[3,5]
PETN[a]	0.34	0.19	[3,5]	-0.18	0.05	[3,5]
	0.85	0.06	[4,5]	-0.11	0.04	[4,5]
CMC-Silver azide				-0.42	0.16	[4,5]
Black Powder	1.26	0.15	[4,5]	0.17	0.19	[4,5]
Picric acid(coarse)				>1.4		[4,5]
Picric acid(fine)	0.16	0.11	[4,5]	>1.4		[4,5]
Trinitrotoluene(TNT)	0.83	0.11	[4,5]	>1.4		[4,5]
Nitroguanidine	>1.4		[4,5]	>1.4		[4,5]
Guanidine nitrate	>1.4		[4,5]	>1.4		[4,5]
m-Dinitrobenzene	>1.4		[4,5]	>1.4		[4,5]
Others Dibenzoylperoxide	0.14	0.11	[3,5]	-0.03	0.59	[3,5]
Sporting paper cap	-0.98	0.10	[3,5]	-1.34	0.04	[3,5]
Flat paper cap	-1.36	0.15	[c]	-1.57	0.11	[c]
DPT[a]				>1.4		[4,5]

a) EG : Ethyleneglycol, CEL : Cellulose powder (passed 300 mesh),

As_4S_4 : Realgar, DDNP : Diazodinitrophenol, PETN : Pentaerythritol tetranitrate, DPT : Dinitrosopentamethylenetetramine

b) The value transformed from reference No.6.

c) unpublished data

References of Table 3.8

1) Yoshizawa F., Inoue Y., Kaneko Y., Matsunaga T., Tamura M., Kuramochi I. and Yoshida T. , Jour. Safety Engineering, Japan, 26, 283(1987)

2) Inoue Y., Yoshizawa F., Matsunaga T., Kaneko Y., Tamura M., Hirayama T., Kuramochi I. and Yoshida T., Nippon Kasai, Japan, 36, 9(1987)

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height in this context means the height of drop hammer where the sample has a 50% probability of exploding.

In the case of the drop hammer test using the up and down method, the drop height is decreased at certain intervals when the sample explodes or correspondingly is increased at certain intervals when the sample dose not explode. This procedure is carried out through several iterations. As the result of these trials, test heights are concentrated near the 50% explosion height, and it becomes possible to estimate the 50% explosion height.

In Germany the 1/6 explosion height has conventionally been used. The 1/6 explosion height is the height where one "go" occurs in 6 repeated trials. The basic idea behind this method is as follows. The sensitivity near the height where no explosion occurs (i.e. where sample does not "go") should be determined. If the 50% explosion height is the height where half of the tests are positive, the 1/6 explosion height is the height where the 17% of tests apparently are positive. Therefore the 1/6 explosion height is near the point where no explosions take place. It may not be possible to finish the test with fewer trials than are used in the up and down method, because a minimum number of seven trials is required. This method has the advantage that it can measure a wider sensitivity range with just the 5kg drop hammer than is possible with the up and down method.

The method of measuring the 1/6 explosion height suffers from poorer reliability and unknown accuracy when compared with 50% explosion height measurement with the up and down method.

3.3.3.2 Up and down intervals: the intervals in the fall height with the same distance and the same logarithm distance.

When the results are analyzed after the trials with the up and down method, it becomes problematical to make the intervals of the fall heights the same size or to make the logarithms of integrals of the fall height the same. Professor Dixon et al. described that, in the case of sensitivity data for explosive substances, the distribution of the probability of explosion becomes closer to a normal distribution when the logarithm of the fall height is used rather than the fall height itself. In the up and down method, the analysis is done under the supposition that the distribution of explosion probability is a normal distribution.

Figure 3.11 shows the distribution of the accumulated explosion ratio frequencies for a drop ball test using sport paper caps 24) . Test trials at each fall height are done 30 times; (a) is the case where the fall heights are taken at the same interval and (b)is the case where the logarithms of the fall heights are taken at the same interval. Apparently the case where log H is taken with the same intervals shows better linearity and is nearer to a normal distribution.

The standard deviation (σ) of a normal distribution is also presumed for trials for the 50% explosion height (H_{50}) with the up and down method. The 1/6 explosion height can be estimated using these two values. Accordingly it seems better to use the up and down method to find the 1/6 explosion height.

The next problem is to determine an adequate up and down interval.Dixon indicated that the interval near σ is adequate and should be in the range of 0.5–2.0 σ 21) . The impact sensitivity of the sport paper caps had a narrow deviation range, and it was observed that the distribution was nearer to a normal logarithmic distribution. However, common explosive substances do not always behave this way. Figure 3.12 shows an example.

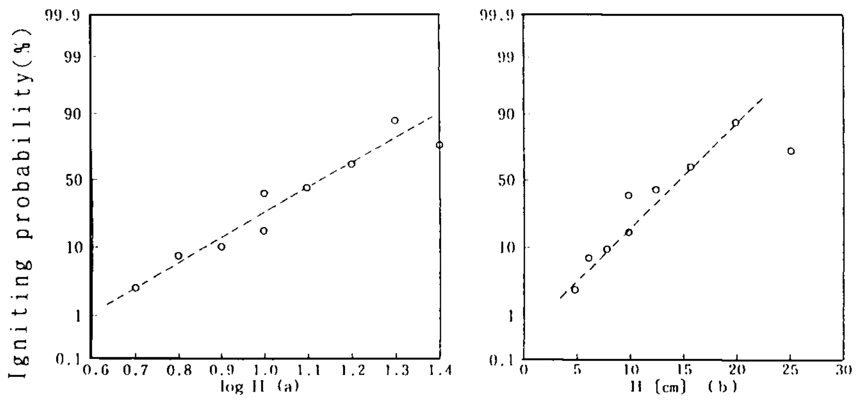

Figure 3.12 The accumulated explosion rate plotted on semi–log paper in normal and logarithm scale with contacting mixture of potassium nitrate and red phosphorus using direct impact method

3.3.3.3 Sample settling: influences of direct impact, indirect impact and the roller used for indirect impact

The amount of energy necessary to cause ignition or explosion of the sample varies with the size and composition of the roller placed on the sample. The various sizes and compositions of roller tested in the indirect impact method are shown in Figure 3.13.

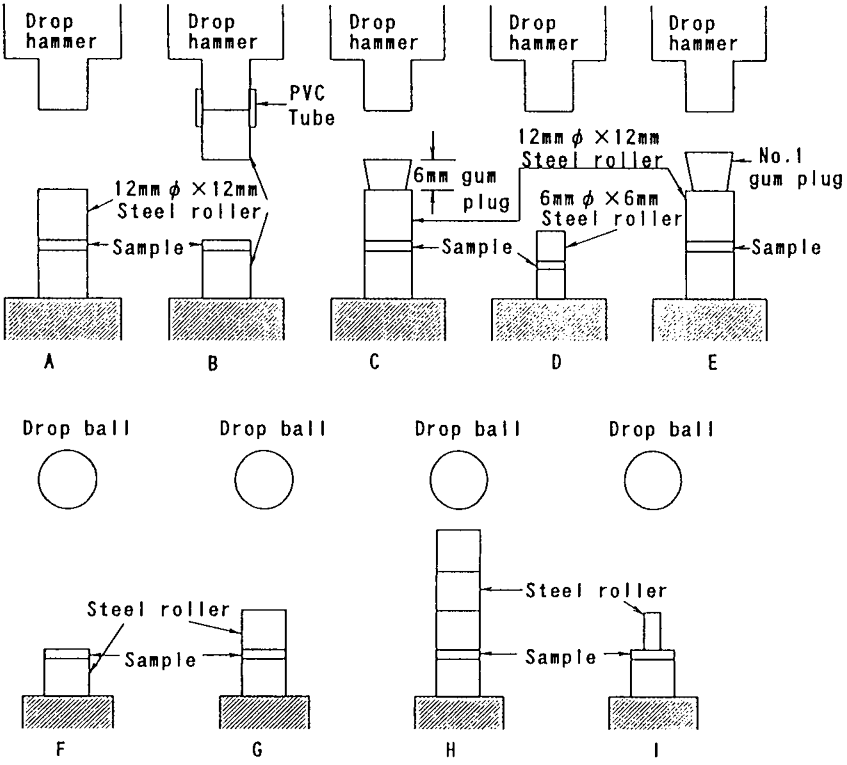

Fig. 3.13 The sample structure for drop ball and drop hammer

Methods A to E are drop hammer tests and F to I are drop ball tests. The order of amounts of energy necessary for explosion to occur is:

E > C > A > B > D

When results of the drop ball test are included, this order becomes:

H > A > G > I > F

As described above, an explosion occurs in response to lower energy when a direct impact is given. Direct impact is more convenient because it is possible to run tests with lighter balls. Another problem does arise in that certain explosive substances detonate in response to indirect impact but do not explode with direct impact. In these cases, direct impact cannot be used. The reverse case is also known to occur.

Certain substances have smaller deviations in direct impact tests than in indirect tests, and once again the reverse case also occurs (referred to in Figure 3.14).

From these observations, the author and others consider that the direct impact test should first be done for certain samples, and if no explosion occurs or the deviation in data is large (in the case of large σ) the indirect impact drop ball sensitivity test should be done. If no explosion occurs by the indirect impact method, it is recommended that the variable initiator weight test with ballistic mortar [27] or the small gap test [28] be carried out.

In Japan, the Japanese Fire Services Law was revised, and the classifications of dangerous goods according to adequate tests have been proposed [31] . Under these proposals solid oxidizers should be put into contact with red phosphorus and the mixtures should be tested with the drop ball impact sensitivity test. After that they may be classified. As standard oxidizers, solid potassium chlorate and potassium nitrate were selected. As the mixture of potassium nitrate and red phosphorus shows an unreasonably high 50% explosion energy (Figure 3.14) upon indirect impact, the direct impact method [29] was recommended. Taking the direct impact method, it is convenient to use a drop ball with a weight of 260g. Otherwise, the intimate mixture of potassium chlorate and red phosphorus is so sensitive that it is impossible to measure the sensitivity accurately with the direct impact method. Accordingly the authors recommend using the indirect impact method [32] .

In the case of the indirect impact method, the size of the steel roller placed on the sample influences the test results. As shown in Figure 3.15, if the steel roller used is small, the apparent sensitivity becomes higher. However, it is recommended that a steel roller 12mm in diameter and 12mm high be used to carry the sample; this size has been used as a general case because the delivery of the impact becomes more unreliable as the size of the steel roller becomes smaller.

3.3.3.4 The influence of the mass of the drop ball [24]

An example of test results which illustrate the influences of drop ball weight is shown in Figure 3.16. If the average values are compared, the test results with a drop ball weighing 250g are most sensitive. But after error analysis it seems that the test results of the drop ball impact sensitivity test do not depend on the weight of the ball. Deviation becomes larger when lighter balls are dropped from greater height. Also in this situation, judgment of variations in sounds becomes impossible because of the louder sound made by the impact of the drop ball against the steel roller. According to the experiences of the author et al., the selection of the drop ball weight should be made to get the H_{50} value as close to 10cm as possible.

Similar test results for intimate mixtures of potassium nitrate and red phosphorus [29] , potassium chlorate and red phosphorus [32] and potassium chlorate and sulfur [32] are

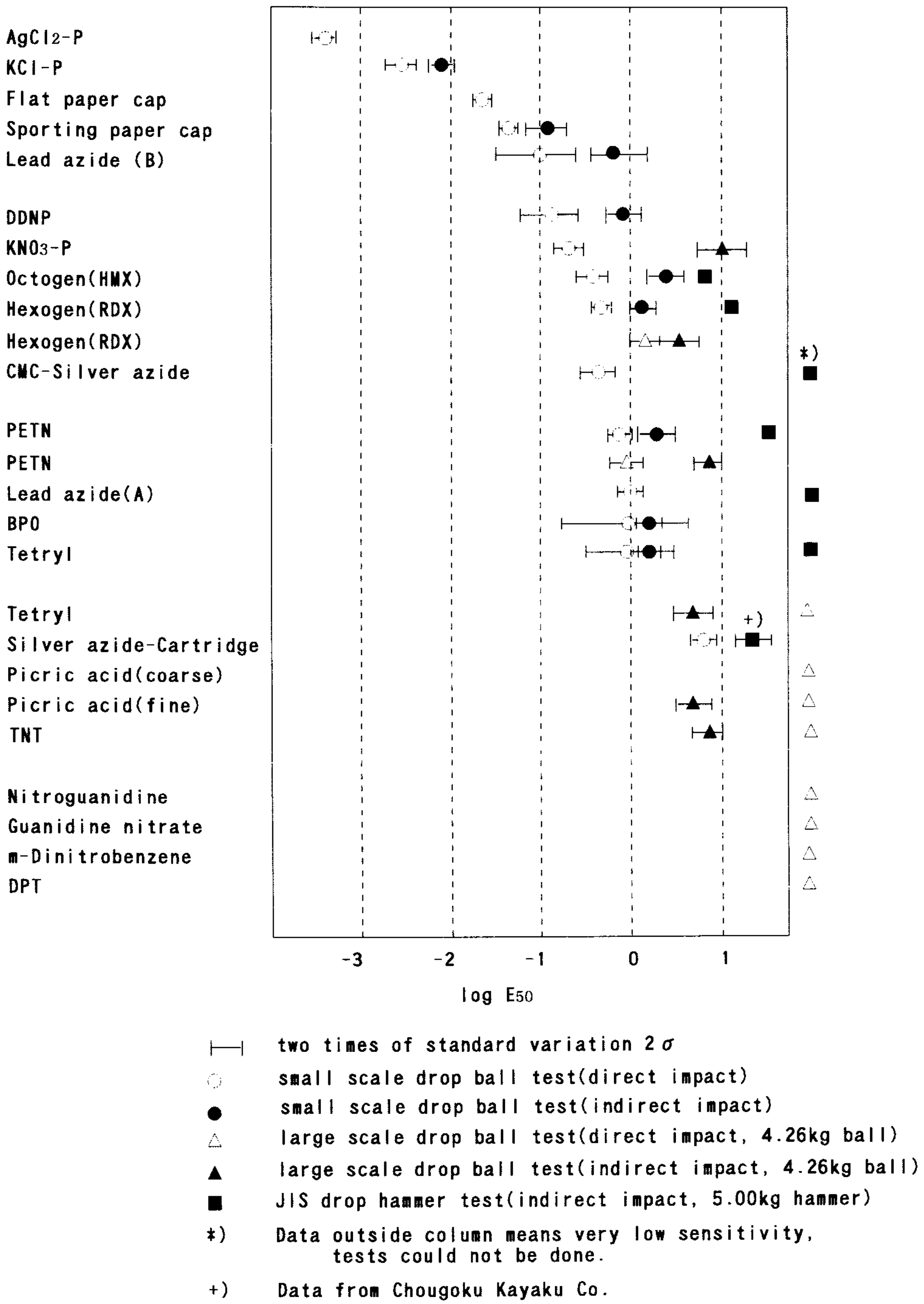

Fig. 3.14 The log(E_{50}) of explosive substances and samples for drop ball and drop hammer tests

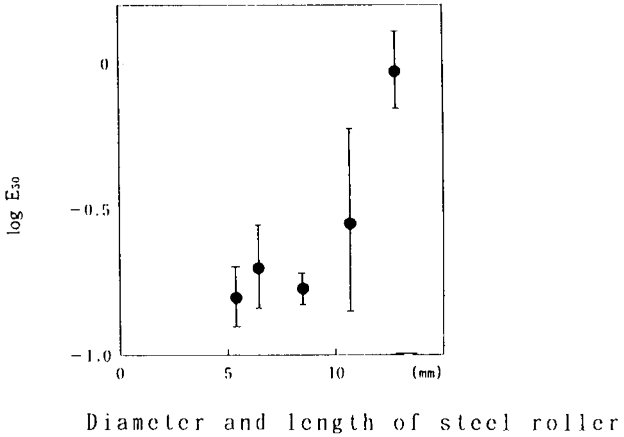

Fig. 3.15 The influence of upper roller size in indirect impact test

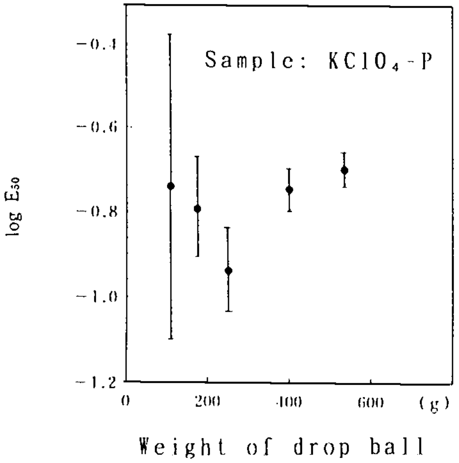

Fig. 3.16 The influence of drop ball size in this impact test

already known. Test results for the latter two are shown in Figure 3.17. Mixtures of potassium chlorate and sulfur apparently show small deviations, but actually it is difficult to judge "go" or "no go" because no sound or fire occurs.

3.3.3.5 The influence of particle size

Lump samples are less sensitive than powder samples. Large particle sized picric acid does not "go" when a 5kg ball is dropped from a height of 100cm in either the direct or indirect impact methods, but fine particle sized material pulverized in an agate mortar will "go" when a 5kg ball is dropped from only 10cm in the indirect impact method.
Judgments are possible with the direct impact method. In the case of the intimate mixture of potassium nitrate and red phosphorus, results with higher sensitivity were achieved as smaller particles of potassium nitrate were used, as shown in Table 3.9.
Otherwise the opposite tendency is observed for mixtures of potassium chlorate and red phosphorus. That is, log H_{50} = 0.45 and σ =0.14 were recorded when extra grade reagent potassium chlorate was used at it was, but log H_{50} = 0.79 and σ = 0.17 were recorded when the potassium chlorate was pulverized in an agate mortar. The reason for this occurrence is that the highly sensitive oxidizers like potassium chlorate have highly reactive surfaces; when their crystals are broken upon impact, the surfaces react with red phosphorus. Meanwhile impact does not create new surfaces on pulverized oxidizers. Less sensitive oxidizers like potassium nitrate do not have highly reactive new surfaces, but larger areas of contact with red phosphorus seem to be advantageous for the reaction.

3.3.3.6 Mixed state : mixing in a mortar and contact mixing

The author et al. measured the impact sensitivity of mixtures of oxidizer and red phosphorus to investigate the relative impact sensitivity to oxidizer composition 22, 23, 25). As some oxidizers and red phosphorus mixtures have extremely high sensitivity, an ordinary mixing operation can be dangerous. Accordingly we carried out these tests by putting the compounds together (intimate mixing) without physical mixing. However, it is necessary to know the relationship between the sensitivity of a simple contact mixture and that of a physically mixed or perfect mixture. Though the mixture of potassium nitrate and red phosphorus is relatively insensitive compared to other mixtures of oxidizer and red phosphorus, we mixed them carefully in an agate mortar to achieve a perfect mixture and carried out the tests with it. Test results are listed in Figure 3.18, which shows the data for contact mixtures. Though the perfect mixture has a higher sensitivity than the simple contact mixture, the difference is 0.02−0.21 on the log H scale. These differences are not large in light of the deviation. Accordingly it is thought that the impact sensitivity of the mixture of potassium nitrate and red phosphorus is measured with sufficient accuracy using the simple contact mixture. The deviation in the data is smaller with the perfect mixture. With respect to the mixing ratio, a value near 50/50 showed the highest sensitivity in the range of our tests.

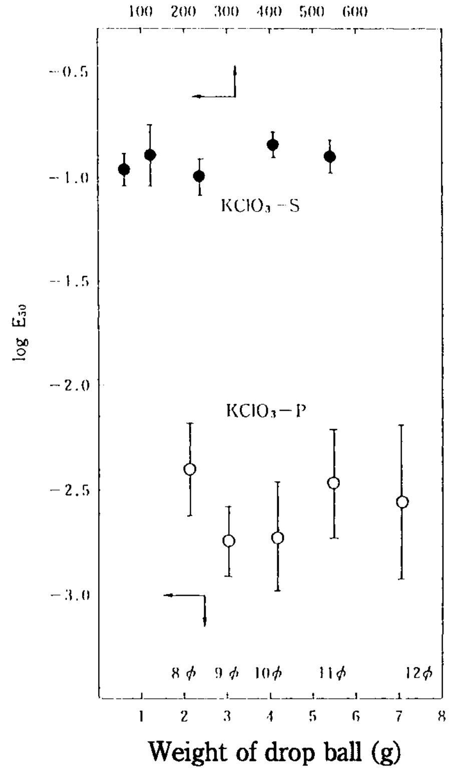

Figure 3.17 The influence of drop ball size for contacting mixture of potassium chlorate and red phosphorus (○) and that of potassium chlorate and sulfur (●)

3.3.3.7 The influence of water

Some investigations examining the influences of water on the data are known. According to these, small amounts of water do not drop the sensitivity of explosive substances but increase it in many cases. Many explosive substances become insensitive when they contain large amounts of water. However in terms of actually proving these assertions, the drop ball impact sensitivity test is not sufficient. This test should be done in combination with the variable initiator weight test 27) or the small gap test 28) . It is difficult to observe the influence of water in the drop ball impact sensitivity test alone. Because the sample weights for the drop ball impact sensitivity test are small (4–12mg), the samples may become too hygroscopic or too dry during the treatment in air.

3.3.3.8 Regarding the use of red phosphorus in the evaluation of oxidizers

Contacting mixtures of oxidizers and red phosphorus are used for the classification of dangerous properties of oxidizers. The properties of the red phosphorus used in these tests are also important. The author et al. have retained it in desiccators with silica gel prior to use. We did not have any concern about its particle size, because it is relatively soft and is rubbed on the steel rollers to coat them. However it has been found that the properties of the red phosphorus also influence the measured results.

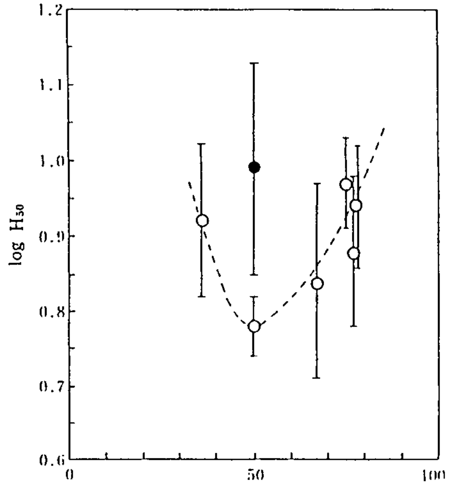

Figure 3.18 The influence of sample mixing state log(H50) versus potassium nitrate concentration for perfect mixture of potassium nitrate and red phosphorus (○); the data from a contacting mixture (●) is also plotted.

One example is shown in Table 3.10. These results were recorded using potassium nitrate and two kinds of red phosphorus. The data are coincident within the range of the deviation [29] . Other test results were recorded with old reagent red phosphorus (C) which was opened several decades before a new sample (A). The results are shown in Table 3.11. The simple contacting mixtures using the old red phosphorus did not explode with a loud noise; this indicates that the old red phosphorus has apparently changed.

3.3.3.9 The sound of the explosion

Some substances make a loud sound upon exploding and others hardly make a sound in drop ball impact sensitivity tests. The simple contact mixture of potassium chlorate and red phosphorus is one of the substances which makes loud sound when exploding. About a 100dB (A−fast) noise is measured at a distance of 3m. The frequency distribution is shown in Figure 3.19 [32] . However the mixture does not always make the same explosive sound; sometimes it makes softer sound, and other times, no sound at all. Sporting paper caps and toy paper caps cause loud noises with narrow frequency

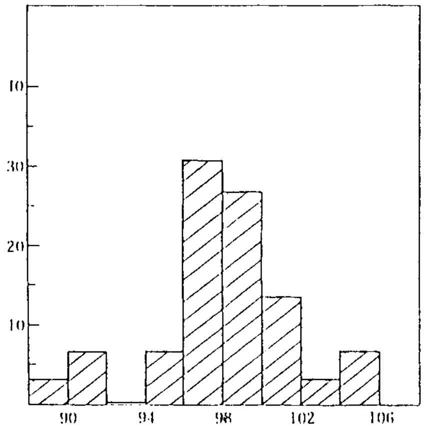

Figure 3.19 The noise level (A fast) at 3m distant point using contacting mixture of potassium chlorate and red phosphorus with direct impact method. The weight of each component is about 6mg

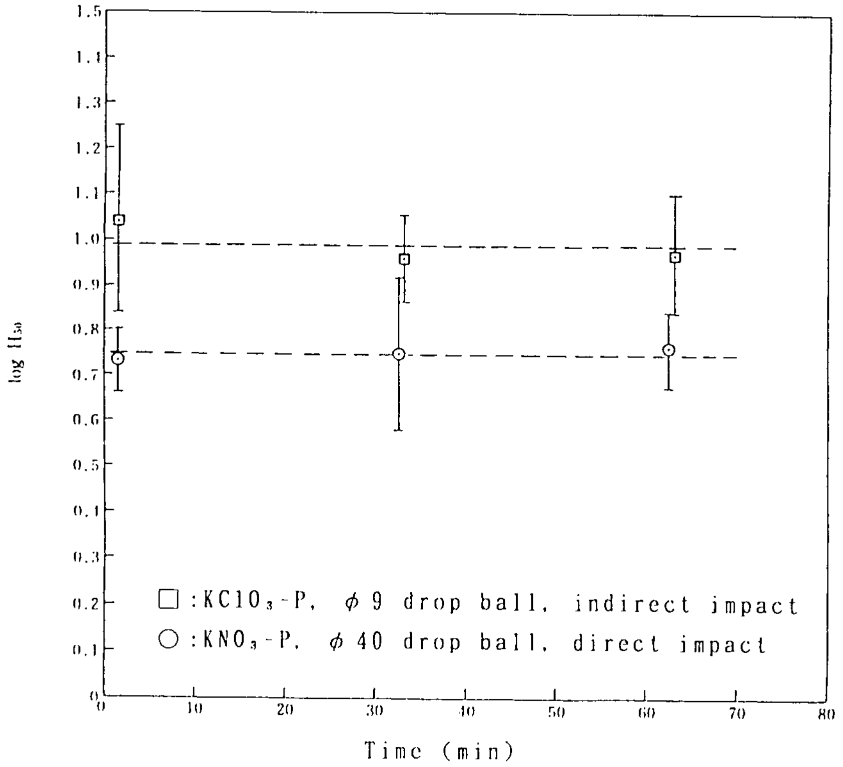

Figure 3.20 The influence of time from mixing to measuring using mixtures of potassium nitrate or potassium chlorate and red phosphorus

Table 3.9 The results of drop ball test for using various particle size of potasium nitrate (Direct impact method using 255g of steel ball)

ITEM	made by "WAKO" ground by an agate motar	made by "OTUKA" smaller than 140 mesh	made by "OTUKA" particle size between 24 and 100 mesh
H_{50}(cm)	9.8	12.0	14.1
log E_{50}	-0.62	-0.52	-0.45
σ	0.14	0.14	0.15
E_{50}(J)	0.24	0.30	0.35

Table 3.10 The results of drop ball tests for potasium nitrate and red phosphorus contacting mixture using 2 kinds of red phosphorus (Direct impact method)

weight of drop ball (g)	ITEM	red phosphorus (A) made by "KOSO KAGAKU"	red phosphorus (B) made by "WAKO JUNYAKU"
225	H_{50}(cm)	11.6	15.0
	log E_{50}	-0.59	-0.49
	σ	0.18	0.05
	E_{50}(J)	0.26	0.32
255	H_{50}(cm)	9.8	8.5
	log E_{50}	-0.62	-0.67
	σ	0.14	0.10
	E_{50}(J)	0.24	0.21

Table 3.11 The results of drop ball tests for potasium chlorate and red phosphorus contacting mixture using old and new red phosphorus (Indirect impact method using 9mm diameter and 2.97g weight steel ball)

ITEM	old red phosphorus (C)	new red phosphorus (A)
H_{50}(cm)	15.5	5.5
log E_{50}	1.19	0.74
σ	0.21	0.12
E_{50}(J)	0.0045	0.0016
noise level (dB)	no explosive sound	large explosive sound 100 (dB)

distributions because of their performance [20].

As lead azide, silver azide, diazodinitrophenol(DDNP) and others also make loud explosive sounds, we could judge them "go" or "no go" on the basis of the sound. The noise level with the drop ball impact sensitivity test with oxidizers and flammable mixtures is shown in Table 3.12 33).

3.3.3.10 Changing sample quality with time

Changes in quality with time for mixtures of oxidizers and red phosphorus were also investigated 33). As the results show in Figure 3.20, no changes are found over a one hour period.

Table 3.12 The noise level at point which is distant 3m from test equipment for drop ball test(S dB(A fast)).

Explosive substances	Impact method	Ball weight (g)	Fall height (cm)	S dB (A fast)	
				"go"	" no go"
$KClO_3$-P	indirect	2.97	6.2	98	<60
$KClO_3$-S	direct	111	10.0	70	67
$KClO_3$-C a)	direct	535	10.0	71	74
$NaClO_3$-P	indirect	2.97	5.5	98	<60
$NaClO_2$-P	indirect	2.97	5.5	97	<60
$NaBrO_3$-P	indirect	2.97	5.5	94	<60
$KBrO_3$-P	indirect	2.97	5.5	96	<60
$Ba(ClO_3)_2 \cdot H_2O$	indirect	2.97	5.5	100	<60
$KClO_4$-P	direct	261	5.2	103	66
$LiNO_3$-P	direct	261	5.2	66	66
$NaNO_3$-P	direct	261	5.2	69	66
NH_4NO_3-P	direct	261	5.2	64	66
CaO_2-P	direct	261	5.2	66	66
KNO_3-P	direct	261	5.2	68	66

a) C is cellulose type C

3.3.3.11 Sensitivity and reactivity change with impact

The simple contacting mixture of potassium chlorate and red phosphorus becomes more sensitive when it is shocked once and does not explode. Also the mixtures were more reactive with water. If the water was poured on the mixtures that had been shocked once, they sometimes ignited.

3.3.4 Precautions to take when measuring

(1) The indirect impact method is used for highly sensitive substances. The careful placement the sample between two steel rollers is necessary. The weight of the

sample should be limited to several miligrams, and large weights of sample should not be tested.

(2) As highly sensitive substances make loud noises, sample weight should be limited.

(3) When the sample does not explode, the sample should be wiped off after the rollers are placed in water. However, as some substances are water reactive, previous testing on a small quantity of sample is necessary.

(4) Earplugs, safety gloves and goggles should be available. Partical ventilation equipment should be used because harmful smoke like phosphorus oxide may be emitted when a sample ignites.

(5) A 9mm diameter drop ball sometimes may not drop because it has been magnetized by the test apparatus. In this situation, the magnetic field should be reduced by using a slidac.

(6) As red phosphorus degrades over time, a standard substance should be measured whenever the kind of red phosphorus used or the measuring date is changed. As there are individual variations in sample preparation or in placing the sample on the anvil, the same operator should carry out all tests against a standard substance during a series of drop ball tests.

3.3.5 Problems and their solution

When impact sensitivities of explosive substances are measured with the drop ball or drop hammer impact sensitivity test, problems that one may encounter and suggestions for their solution are as follows.

(1) Some samples do not explode with the drop ball or drop hammer impact tests even though they have essentially high sensitivity. There may be doubts that such samples are highly sensitive substances based on their chemical structure or on a general knowledge of explosives.

(2) Generally, a sample becomes more sensitive as its particle size becomes finer; the test should be done after pulverizing the sample in an agate mortar when coarse particles do not explode at 100cm with 5kg.

(3) Sometimes an explosion will not occur or the deviation becomes larger as a function of the impacting technique (direct or indirect impact). In these cases the other impacting method should be used for testing.

(4) As the errors are larger in the conventional method of determining the 1/6 explosion height, it is recommended that the up and down method be used with the same logarithmic intervals for the fall heights as are applied in the determination of the 50% explosion height. It is possible to get 1/6 explosion height with a standard deviation from those data.

(5) Generally explosive substances are more insensitive in packaged products than in raw powder. However if the formulation is not complete, it often becomes more

dangerous. For example a fire occurred involving the sporting paper cap from a box which had been opened. The reason for the fire was thought to be that the red phosphorus, sulfur and potassium chlorate mixed powder released from the package ignited as a result of friction.

3.3.6 The order of sensitivity for highly sensitive substances

Impact sensitivity tests only measure the 50% explosion height with simulated percussive forces and only indicate the explosive energy under those conditions. Recorded values change with the measuring equipment or the measuring method. Accordingly it may be better to indicate relative sensitivities using the same equipment and the same measuring method and to include standard explosive substances in the listing. Figure 3.14 shows the order of measured sensitivities for some explosive substances. Simple contact mixtures of silver chlorate and red phosphorus showed the highest sensitivity among those measured. Lead azide and DDNP, which are primary explosives, showed sensitivity similar to secondary explosives like PETN or RDX. However, once primary explosives ignite, they accelerate easily to detonation (DDT). Accordingly, primary explosives are more dangerous than secondary explosives like PETN or RDX.

The commercial products, sporting paper caps (SPC : potassium chlorate, red phosphorus and sulfur), toy paper caps (same components as SPC) and silver azide cartridges for breaking renal calculi have lower sensitivity than their powdery components because they are packaged as cartridges.

Also packaged SPC only burn and do not detonate when they are on fire. Safely packaged SPC are separated by buffering materials between the SPC boxes so that fire will not propagate from one to the other once initiated. As these examples illustrate, there are many ways to make explosives safer by segregating small portions by effective packaging.

3.3.7 The drop ball type impact sensitivity test (C): established in the Japanese Fire Services Law; Classification test for Class 1 oxidizer solids as decided by the Japanese Fire Services Law

(1) The object of this test

This test seeks to evaluate the sensitivity of solid substances to impact. For these purposes, the 50% explosion height (where the explosion occurs at 50% probability) is measured by dropping a steel ball onto a standard mixture made of some standard substance and a flammable substance. The sample is judged "go" (for explosion) or "no go" (for no response) at 50% probability by dropping the same steel ball onto a sample mixture made with sample in question and a flammable substance from the same height used with the standard.

(2) Standard substances and flammable substance

(A) Standard substances

Standard substances are potassium chlorate[*1] (adapted by JIS as an extra pure reagent) and potassium nitrate[*2] (adapted by JIS as a guaranteed reagent), and the particle size of each must be such that it passes through a standard 300 μm sieve (about 50 mesh) and does not pass through a 150 μm sieve (about 100 mesh). Standard substances should be held more than 24 hours in a desiccator with silica gel for drying.

(B) Flammable substance

The flammable substance is red phosphorus powder[*3] (adapted by JIS as an extra pure reagent). Its particles should pass through a standard 180 μm sieve (about 80 mesh). The flammable substance should be held more than 24 hours in a desiccator with silica gel for drying.

(3) Sample goods

The goods are tested in whatever shape they appear in the marketplace. If they include some lumps, however, the test should be run on that portion that passes through a standard 1.18mm sieve (about 14 mesh). The test sample should be held more than 24 hours in a desiccator with silica gel for drying.

(4) Test place

The place for these tests should be an inner room where the temperature is 20 ± 5 °C, the moisture is 50 ± 10% and ventilation to the atmosphere exists.

(5) Test method

(A) The test method for standard substances

(a) Potassium chlorate

(a.1) Charging of sample

About 2mg of red phosphorus is placed on a steel roller 12mm in diameter and 12mm in height[*4], and about 2mg of potassium chlorate is placed on the top of it. A steel roller with the same shape is carefully placed on the top.

(a.2) The method using a dropping steel ball

A steel ball 7mm in diameter[*5] (about 1.4g) is dropped onto the upper steel roller to provide a percussive shock to the samples from a height of $H = 10$cm[*6] ($\log H = 1.0$). The samples are graded as "go" or "no go". The samples which explode and emit sound, fire and smoke are judged a "go" (they react).

This test should be repeated more than 40 times[*7, *8] iteratively with the up and down method; the fall height is decreased when the samples "go", and it is increased when "no go" is the judgment. After this is completed, the 50% explosion height[*9] should be determined. For this test, the difference between the logarithms of the individual fall heights should be 0.1; also the 50% explosion height should be in the range of 0.5 to 2.0 times[*10] the standard deviation of the logarithm of fall height determined from the test results.

(b) Potassium nitrate

(b.1) Charging of sample

5mg of red phosphorus is placed on a steel roller 12mm in diameter and 12mm in height. Then 5mg of potassium nitrate are placed on the top of it. An upper roller is not used.

(b.2) The method of dropping a steel ball

The 50% explosion height (H_{50}) should be determined using the same procedure as (a.1). In this case, the steel ball 40mm diameter (about 261g) should be used.

(B) Test method for goods

(a) Comparison with potassium chlorate

(a.1) Charging of sample

Same as A(a.1).

(a.2) The method of dropping a steel ball

The steel ball used in A(a.2) is dropped 10 times at the 50% explosion height determined in A(a.2). If the responses are all "go", the test is finished. [Case A]

If the responses were all "no go", test B(b) as shown in the following should be done. If "go" and "no go" were observed in the tests 10 times, an additional 30 trials should be done (total 40 times). [Case B]

(b) Comparison with potassium nitrate

(b.1) Charging of sample

Same as A(b.1).

(b.2) The method of dropping a steel ball

The steel ball used in A(b.2) is dropped 10 times at the 50% explosion height determined in A(b.2). If the responses are all "go", test is finished. [Case C]

If the responses are all "no go", the test is finished. [Case D]

If "go" and "no go" were observed in 10 tests, an additional 30 trials should be done (total 40 times). [Case E]

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*1 potassium chlorate (reagent) : JIS K 8207−1961

*2 potassium nitrate (reagent) : JIS K 8548−1975

*3 red phosphorus (reagent) : JIS K 8595−1961

*4 roller : JIS B 1506−1976 with no distortion in the center of flat surface

*5 steel ball : JIS B 1501−1983

*6 fall height : When an upper roller is used, it is the distance between the lower end of the ball and the upper surface of the top roller. When an upper roller is not used, it is the distance between the lower end of the ball and the upper surface of the roller.

*7 40 times : These counts start at the transition from "go" to "no go" or the reverse.

*8 : When the roller is reutilized, it is used after its surface has been polished with No.600 sandpaper adapted by JIS R 6252−1976.

*9 The 50% explosion height is determined in the next section.

*10 If the deviation is outside this range, the test should be run again.

(6) Judgment

The grades of sensitivities for tested goods are as follows in response to each case described in B(a.2) or B(b.2).

Case A : Rank I
Case B : Rank I if "go" is recorded 20 or more times
Rank II if "go" is recorded fewer than 20 times
Case C : Rank II
Case D : Rank III
Case E : Rank II if "go" is recorded 20 or more times
Rank III if "go" is recorded fewer than 20 times

The complete judgement for Class 1 dangerous goods is made with the "Combustion test" results (See 3.5.2). The goods which were classified in Rank III have a possibility of being excluded from the list of dangerous materials.

3.3.8 Previous investigations with the drop ball impact sensitivity test established in the Japanese Fire Services Law : 10/20 drop ball impact sensitivity test (D)

The drop ball test established in the Japanese Fire Services Law is thought to be a rational test method, but before reaching this decision, a similar and simpler test method was investigated [33]. In conclusion, for such investigations the quantity of oxidizing solid on the border line of activity should be increased in the test trials. However it may be useful to recognize the property of the drop ball test as established in the Japanese Fire Services Law to show those data.

D1. Name of test method

10/20 drop ball impact sensitivity test

D2. Property to be tested

Is a simple contact mixture of a sample oxidizer and red phosphorus more or less sensitive than mixtures of potassium nitrate and red phosphorus or of potassium chlorate and red phosphorus.

D3. Test equipment

Small sized drop ball test equipment (previously described)

D4. Test procedure

D4.1 Measuring the H_{50} (cm) for a mixture of potassium nitrate and red phosphorus

(1) Approximately 5mg of red phosphorus is rubbed on a roller 12mm in diameter and 12mm in height as prescribed in JIS B 1506.
(2) Approximately 5mg of potassium nitrate pulverized in an agate mortar is sprinkled on this.
(3) The steel roller is quickly placed on the anvil of the drop test equipment.

(4) A steel ball 40mm diameter and 261g in weight as prescribed in JIS B 1501 is held at 10cm height (logarithm scale 1.0) by the electromagnet.

(5) The steel ball is dropped on the mixture of potassium nitrate and red phosphorus by cutting off the switch of the magnet.

(6) If the sample is a "go", the fall height is decreased by the interval of $\triangle \log H = 0.1$. When the sample is a "no go",the fall height is increased by same interval.

(7) The up and down iteration is carried out as in the previous experiment when the first "no go" is observed by decreasing the height or when the first "go" is observed by increasing the height.

(8) In the case of the up and down method, the tests are continued by raising the height at the interval of $\triangle \log H = 0.1$ when the sample is a "no go" and by decreasing the height at same interval when the sample is a "go". A total of 20 tests should be done.

(9) The test results are analyzed and the 50% explosion height (H_{50}) as well as standard deviation (σ) of log H determined.

D4.2 The impact sensitivity test for classifying the oxidizer and red phosphorus contact mixtures of low sensitivity

(1) Samples should be made by the same method as the potassium nitrate and red phosphorus contact mixture.

(2) The same steel balls are dropped from the height of H50(cm) determined in the above test and the number of "go" observations in 20 trials is recorded.

(3) The samples which are "go" more than 10 times are judged to be more sensitive than the potassium nitrate and red phosphorus contacting mixture.

D4.3 Measuring the H_{50} (cm) for the contacting mixture of potassium chlorate and red phosphorus

(1) Approximately 2mg of red phosphorus is rubbed onto the upper surface of a roller 12mm in diameter and 12mm in height as prescribed in JIS B 1506.

(2) Approximately 2mg of potassium chlorate pulverized in agate mortar is sprinkled on this.

(3) This steel roller is placed quickly on the anvil of the drop test equipment. An identical roller is placed on top of it.

(4) A steel ball 9mm in diameter and 2.97g in weight as prescribed in JIS B 1501 is held at 10cm height (logarithm scale 1.0) by an electromagnet.

(5) The steel ball is dropped on the upper roller by cutting off the magnet switch.

(6) When the sample is a "go", the height of the drop is decreased by the

interval of $\triangle \log H = 0.1$. When the sample is judged a "no go", the height of the drop is increased by the same interval.

(7) The up and down iteration is carried out as in the previous experiment when the first "no go" is observed and the height is decreased, or when the first "go" is observed and the height is increased.

(8) In the case of the up and down method, tests are continued by raising the height at the interval of $\triangle \log H = 0.1$ and by decreasing the height at the same interval. A total of 20 tests are done.

(9) Test results are analyzed and the 50% explosion height (H_{50}) as well as standard deviation (σ) of log H determined.

D4.4 Impact sensitivity test for classification based on the mixture of highly sensitive oxidizer and red phosphorus.

(1) The samples should be made with same method as the potassium chlorate and red phosphorus mixture.

(2) The same steel balls are dropped from the height of H_{50} (cm) as determined in above test and the number of "go" events in 20 trials is recorded.

(3) The sample which yields "go" more than 10 times is judged to be more sensitive than the mixture of potassium chlorate and red phosphorus.

D4.5 Data treatment The data treatment for the up and down method is done by the method described in 3.3.1, B4.1.3.

D5. Examples of test results

D5.1 The 50% explosion heights (H_{50}) for the mixtures of potassium nitrate and red phosphorus and of potassium chlorate and red phosphorus

The results are shown in Table 3.13. The test results using the up and down method for the mixture of potassium nitrate and red phosphorus were that the $\log H_{50}$ is 0.72 ($H_{50} = 5.2$cm) and $\sigma = 0.15$. The test results using the up and down method for potassium chlorate and red phosphorus were that $\log H_{50}$ is 0.74 ($H_{50} = 5.5$cm) and $\sigma = 0.12$.

D5.2 Impact sensitivity test for the classification of mixtures of less sensitive oxidizers and red phosphorus

Drop ball tests were carried out 20 times using the same steel ball and drop height determined as mentioned above for some typical low sensitivity oxidizers. The results are shown in Table 3.14. In Table 3.14 only judgments from test results of up and down methods previously reported [23] (See Table 3.8) are shown. The test results from the 10/20 test method coincided with those from the up and down method.

The order of sensitivity was:

$KClO_4 > LiNO_3 > KNO_3 < NaNO_3 > NH_4NO_3 > CaO_2$.

The substances which yielded "go" more than 10 times were potassium perchlorate and lithium nitrate. They are apparently more sensitive than potassium nitrate. The

Table 3.13 Example of test results of drop ball test for contacting mixture of potassium nitrate and red phosphorus and that of potassium chlorate and red phosphorus

		potassium nitrate -red phosphorus		potassium chlorate -red phosphorus	
Impact method		Direct impact		Indirect impact	
Diameter of drop ball		40mm		9mm	
Weight of drop ball		261g		2.97g	
	trials	log H	Judgement	log H	Judgement
The results of observation	1	0.9	○	0.8	×
	2	0.8	×	0.9	○
	3	0.9	○	0.8	○
	4	0.8	○	0.7	○
	5	0.7	×	0.6	×
	6	0.8	×	0.7	○
	7	0.9	○	0.6	×
	8	0.8	○	0.7	×
	9	0.7	○	0.8	×
	10	0.6	×	0.9	○
	11	0.7	○	0.8	○
	12	0.6	×	0.7	×
	13	0.7	×	0.8	×
	14	0.8	○	0.9	○
	15	0.7	○	0.8	○
	16	0.6	○	0.7	○
	17	0.5	×	0.6	×
	18	0.6	×	0.7	○
	19	0.7	×	0.6	×
	20	0.8	○	0.7	×
Base of judgement		Fire, Smoke and Sound (little)		Fire, Smoke and Sound (big)	
Results of Calculation	H_{50}	5.2 cm		5.5 cm	
	$\log H_{50}$	0.72		0.74	
	σ	0.15		0.12	
	$\log E_{50}$	-0.88		-2.8	

Table 3.14 Impact sensitivity test for low sensitive oxidizer and red phosphorus contacting mixture.
(Direct impact method ,the 40mm diameter and 261 g of weight ball droped from 5.2cm height until 20 times repeated)

oxidizer	Judgement		order of sensitivity		sound	
	fire counts	rate of "go"	10/20 test	up and down[23]	observation	mean
$KClO_4$	17	85	high	high	97~106 dB	103dB
$LiNO_3$	14	70	high	high	61~ 79	66
$NaNO_3$	8	40	low	low	66~ 71	69
NH_4NO_3	3	15	low	low	62~ 66	64
CaO_2	1	5	low	low	66	66
KNO_3	8	40	low	−	66~ 71	68

Table 3.15 Impact sensitivity test for high sensitive oxidizer and red phosphorus contacting mixture.
(Indirect impact method ,the 9mm diameter and 2.97 g of weight ball droped from 5.5cm height until 20 times repeated)

oxidizer	Judgement		order of sensitivity		sound	
	fire counts	rate of "go"	10/20 test	up and down[23]	observation	mean
$NaClO_3$	13	65	high	high	95~102dB	98dB
$NaClO_2$	11	55	high	high	92~100	97
$NaBrO_3$	5	25	low	low	93~ 95	94
$KBrO_3$	5	25	low	high	95~ 97	96
$Ba(ClO_3)_2 \cdot H_2O$	1	5	low	low	100	100
$KClO_3$	13	65	low	−	91~101	98

substances for which "go" was recorded fewer than 10 times were potassium nitrate, sodium nitrate, ammonium nitrate and calcium peroxide. Among these substances, ammonium nitrate and calcium peroxide showed the smallest "go" number. Hence, they are considered safe with respect to impact. Sodium nitrate showed "go" fewer than 10 times but had the same number of "go" entries as potassium nitrate, which was the standard substance.

It is necessary to carry out more trials to get the significant difference rigorously between potassium nitrate and sodium nitrate.

D5.3 The impact sensitivity test for the classification of mixtures of high sensitivity oxidizer and red phosphorus

Drop ball tests were carried out 20 times using the same steel ball and drop height determined as mentioned above for some typical high sensitivity oxidizers. The results are shown in Table 3.15.

In Table 3.15 only judgments from test results of the up and down method previously reported 23) are shown. Test results from the 10/20 test method coincided with those from the up and down method except for the case of potassium bromate. The differences with potassium bromate are thought to arise from the large deviation in the data, the actual difference between the two compounds being very small, and the differences between the two types of of impact methods.

The order of sensitivity was:

$NaClO_3 \doteqdot KClO_3 > NaClO_2 > NaBrO_3 \doteqdot KBrO_3 > Ba(ClO_3)_2 \cdot H_2O$.

The substances for which "go" was recorded more than 10 times were sodium chlorate, potassium chlorate and sodium chlorite. Potassium chlorate was tested at a height of H_{50} which had been determined with the up and down method, and the ratio of "go" to "no go" events ratio was 13/20 (65%). A variation of about 3 times should be considered. When the test result are considered with those from the up and down method, the impact sensitivity of sodium chlorate may not be less than that of potassium chlorate.

Meanwhile a significant difference between sodium chlorite and potassium chlorate is not observed. It is necessary to carry out the test more times to see if there is a significant difference between sodium chlorite and potassium chlorate.

The substances for which "go" was recorded fewer than 10 times were sodium bromate, potassium bromate and barium chlorate. They are therefore considered more insensitive than potassium chlorate. Potassium bromate will require further investigation, because it showed the opposite results to those from previous tests 23) .

3.4 The Ignitability Test

3.4.1 Introduction

Ignitability is an important property for the following substances:combustible solids, mixtures of oxidizers and flammable substances, self-reactive substances, combustible mixed gases, flammable liquids, and explosive substances. These substances, which ignite and burn intensively, have a high possibility of causing accidents. On the other hand, nonflammable substances which do not ignite with high-energy ignition sources in the ignitability tests are unlikely to ignite with low-energy ignition sources such as friction or static electricity. Therefore there is little chance of them causing accidents.

The ignitability of a mixture consisting of flammable gases or flammable vapors and air is tested with electric sparks. The minimum ignition energy is used as the ignitability standard 34). This is the smallest value of energy that is sufficient to ignite explosive substances like flammable air - mixtures (a mixture consisting of gases or vapors or a mixture of powdery substances or mists and air).

The following factors are known to affect the value of the minimum ignition energy : composition, temperature, pressure, additives, and oxygen concentration. In general, the minimum ignition energy is said to have the smallest value when the ratio of the chemical stoichiometry from the balanced reaction describing the process to that of the mixtures' composition is almost 1.But this is not universally true. As the rank of hydrocarbons gets higher, their minimum ignition energy actually shows the smallest value when the chemical stoichiometry to composition ratio is over 1.

The minimum ignition energy decreases drastically as the ambient temperature rises. It increases as pressure decreases, and there is a certain pressure above which a substance will not ignite. It increases when some inert gas is added to the air, whereas it decreases when oxygen is added.

Furthermore, the minimum ignition energy varies according to the structure of the flammable substance. For example, a hydrocarbon ignites with 0.1mJ, while hydrogen and acetylene ignite with one order of magnitude less energy than that.

The ignitability of combustible liquids is influenced by both flashpoint and ignition energy of the mixture of the vapor from the liquid and air. The higher the flash point, the lower the ignitability. In case of temperatures higher than the flash point, ignitability is measured by using the minimum ignition energy of an air mixture as the standard. In this text no further mention will be made of the ignitability of gases and liquids. Please consult other technical books 34, 35).

Ignitability of solids is measured by using ignition sources with different types of energy or by changing the contact time with the ignition source. A typical method illustrating the first type is the BAM ignitability test 2), which was discussed in the previous book 1). Another ignitability test uses electric sparks as the ignition source 3, 6), but it will not be mentioned any further as no actual experiments were conducted with it. The method of the U.S. Bureau of Mines 36) is well-known as an illustration of the second type; it is an ignitability test which changes the period of time the ignition source touches the substance being tested.

In this section, two other methods of ignitability testing are introduced. One is for the classification of flammable solids, which was recently adopted in the revised Fire Services Law; the other, for the classification substances of relatively high ignitability. The second one was actually used in our laboratory.

3.4.2 Small gas flame ignitability test (E): Classification test of the class II hazardous substances as per the Fire Services Law.

(1) Purpose of the test

This test enables comparative ignition experiments with easily ignitable solid inorganic substances. The sample is brought into contact with a small gas flame and one observes if ignition occurs.

(2) Test sample

In principle, the shape of the test sample should be the same as the form in which the material appears in the commercial market. However, a massive sample whose volume is larger than $3cm^3$ is standardized to about $3cm^3$ by cutting or crushing. This test sample is held at room temperature for more than 24 hours in a silica gel desiccator.

(3) Test condition

The test condition is as follows: the temperature is 20 ± 5 ° C, humidity is 50 ± 10%, with atmospheric pressure and no air current *[1].

(4) Procedure

Place a test sample $3cm^3$ in size *[2] on an inorganic heat-insulating sheet *[3] which is standardized to more than 10mm thickness and 12-15cm width. A small liquid petroleum gas flame *[4] is brought in contact with the sample for 10 seconds *[5] and is removed from the sample. Observe whether the test sample combusts with a flame or without a flame (combustion without a flame means the test sample is heated to red heat with out flame) *[6]. If combustion is not observed, repeat this test 10 times.

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*1 Use rooms which have ventilation equipment in case toxic gases from combustion are produced. Darken the room if necessary (for example: in case the assessment of combustions is difficult).

*2 In case the test sample is powdered or grain-shaped, place the substance on the sheet in a hemispherical pile.

*3 The heat conductivity of the inorganic heat-insulation sheet shall be below 0.1W/m·K at 0 ° C.

*4 The gas flame is provided by a simple gas lighter. The length of the flame is standardized to 70mm when the lighter is held vertically. If necessary, a stand may be used with the ignition device.

*5 The contact area between the test sample and the flame is 1 to $2cm^2$, and the contact angle is about 30 °.

*6 Continuous combustion occurs when all the sample is completely combusted (either with a flame or with out a flame) within 10 seconds after removing the gas flame from the test sample, or when the combustion continues more than 10 seconds after the same condition.

(5) Assessment of results

Out of all the test samples, those which not only ignite at least once but which also combust even after the small gas flame is removed should be treated as hazardous substances. These should be classified into two categories. One category is for the high ignitability samples, which ignited within 3 seconds. The other is the normal ignitability samples, which ignited in 3 to 10 seconds.

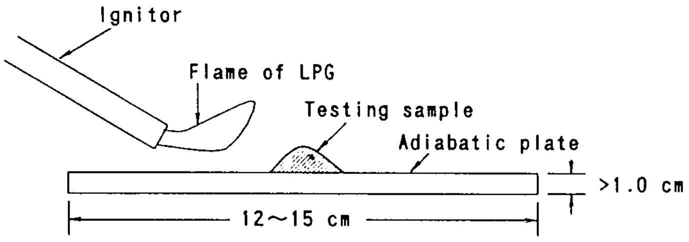


Fig. 3.21 Ignitibility test

3.4.3 The ignitability test for relatively sensitive substances

F1. The name of the test

Cerium/iron spark ignitability test (II)(F)

F2. The property to be tested

Three kinds of substances are ranked according to their ignitability: flammable solids, mixtures of oxidizers and flammable substances, and self–reactive substances.

F3. Apparatus

The same apparatus as the BAM ignitability test: cerium/iron spark (see the previous book [1] p.204). A cerium/iron spark gas lighter is available in Japan as an acetylene–ignition lighter (Trade mark: ROCK). Take about 5mg of sample with a special 5 $\mu\ell$ spatula.

F4. Procedure

The samples are subjected to sparks from a cerium/iron gas lighter (pistol form) for 1 second at a distance of 5mm. The experiment is carried out 20 times and is stopped when the sample ignites.

F5. Data treatment

Record how many times the cerium/iron sparks have been applied.

F6. Assessment of results

The sensitivities of each substance are ranked according to their comparison with the standard substances.

F7. An example of test results

Table 3.16 shows the results of the cerium/iron sparks ignitability test, and the small gas flame ignitability test. Test samples are explosives and contact mixtures of oxidizer and red phosphorus.

Table 3.16 Cerium/iron spark ignitability test; small gas flame ignitability test

Substance	Number of times cerium/iron sparks were applied until substance ignited or results of ignitability	Length of time small gas flame was applied until substance ignited or results of ignitability
$AgClO_3$−red phosphorus	9	
$AgClO_3$−sulfur	5	
Sulfur	no ignition	at once
Red phosphorus	no ignition	at once
$KClO_3$−red phosphorus	13	2 seconds
$KClO_3$−sulfur	no ignition	11 seconds
$KBrO_3$−red phosphorus	4	
$Ba(ClO_3)_2 \cdot H_2O$−red phosphorus	no ignition	2 seconds
$NaClO_2$−red phosphorus	no ignition	2 seconds
HIO_3−red phosphorus	no ignition	1 second
$Fe(ClO_4)_2 \cdot 6H_2O$−red phosphorus	no ignition	3 seconds
$Co(ClO_4)_2 \cdot 6H_2O$−red phosphorus	no ignition	1 second
$LiClO_4$−red phosphorus	11	
$NaClO_4$−red phosphorus	12	
$KClO_4$−red phosphorus	11	
$RbClO_4$−red phosphorus	6	
$Mg(ClO_4)_2$−red phosphorus	no ignition	2 seconds
KIO_3−red phosphorus	no ignition	5 seconds
$K_2Cr_2O_7$−red phosphorus	no ignition	6 seconds
$Na_2Cr_2O_7$−red phosphorus	no ignition	7 seconds
$Ag_2Cr_2O_7$−red phosphorus	17	
$Pb(N_3)_2$	no ignition	5 seconds
DDNP	no ignition	2 seconds
$(NH_4)_2Cr_2O_7$−red phosphorus	no ignition	5 seconds
NH_4IO_3−red phosphorus	no ignition	20 seconds

(Table 3.16 Continue)

Substance	Number of times cerium/iron sparks were applied until substance ignited or results of ignitability	Length of time small gas flame was applied until substance ignited or results of ignitability
$Ba(IO_3)_2$−red phosphorus	no ignition	10 seconds
$NaIO_3$−red phosphorus	no ignition	4 seconds
$K_2Cr_2O_7$−red phosphorus	no ignition	
ZnO_2−red phosphorus	no ignition	3 seconds
SrO_2−red phosphorus	no ignition	10 seconds
MgO_2−red phosphorus	no ignition	10 seconds
BPO	no ignition	4 seconds
Starting signal caps	no ignition	8 seconds
$KClO_4$−red phosphorus (H_2O 20%)	no ignition	7 seconds
$KClO_4$−red phosphorus (H_2O 50%)	no ignition	13 seconds
$KClO_4$−red phosphorus (H_2O 70%)	no ignition	15 seconds
$Ba(IO_3)_2$−red phosphorus	15	
PETN	no ignition	10 seconds
Tetryl	no ignition	7 seconds
$KClO_4$−red phosphorus	no ignition	1 second
$AgNO_3$−red phosphorus	no ignition	1 second
Blue color star composition (powder)	4, 4	
Red color star composition (powder)	no ignition	
Golden color star composition (powder)	4, 2	
Twinkle color star composition (powder)	2, 6	
Green color star composition (powder)	4, 4	

3.5 Burning Test

3.5.1 Introduction

The burning test is designed to measure the intensity of combustion. The test becomes more dangerous to run as substance combust more rapidly and more violently. This section deals only with the test methods available in Japan for measuring the intensity of burning of solid self−reactive substances. Readers should consult other papers [34,38] concerning the burning rates of gaseous or liquid substances. Another important method for evaluating this hazard has been described in a paper published by United Nations. [37] The reference for this work is included, although we have not applied the method in our evaluations.

3.5.2 The 30 g burning test(G) : Classification test 2 for Fire Service Low class 1 (powder) − The burning test

(1) Purpose of the test

This test measure the potential for a solid oxidizing substance to increase the burning rate or burning intensity of a combustible substance when the two are thoroughly mixed. Therefore the components of the test sample must be thoroughly mixed when this test is conducted. The oxidizing substance being evaluated mixed with a combustible substance (or fuel) in a 1:1 or a 4:1 ratio by weight, and the burning time of the mixture is compared to that of a stansard sample mixed at a ratio of oxidizer to fuel of 1:1 by weight.

(2) The standard oxidizer and the combustible substance

a. The standard oxidizer

The standard oxidizer is either extra pure reagent grade potassium bromate or guaranteed reagent potassium perchlorate, both of which must meet JIS specifications. The particle size is also standardized between 300 μ m (about 50 mesh) and 150 μ m (about 100 mesh). The standard substance is kept in the silica gel desicator at a room temperature for at least 24 hours.

b. The combustible substance

Low resinous sawdust is prepared as the standard combustible substance, and its particle size is standardized to between 500 μ m (about 32 mesh) and 250 μ m (about 60 mesh). The sawdustis dried at 105 ℃ for 4 hours and is kept in a desiccator with dried silica gel at a room temperature for at least 24 hours.

(3) Test materials

Refer to 3.3.7(3)

(4) Test place

Refer to 3.3.7(4). There should be no air currents around the insulation board in the test chamber.

(5) The test method

A. The test procedure for the standard substance

(a) The preparation of the standard mixture

Mix a 30g of the standard oxidizer and the combustible substance (sawdust) at a ratio of 1:1 by weight. Introduced this sample into a conical cup and placed it as a conical pile on an inorganic adiabatic board that is at least 10 mm thick.

(b) Allow the sample to equilibrate in the chamber.

The standard mixture is allow to equilibrate at the test site for 1 hour.

(c) The method for ignition

A ring of nichrome wire heated to 1000 ℃ by an electric current is used to ignite the sample. The heated wire is brought into contact with the base of the pile. The maximum contact time is 10 sec.

(d) The measurement of the burning time

Combustion is defined as a state of continuous flame, and the burning time is the duration of combustion measured from ignition to the time the flame disappears. No combustion is judged to occur if the flame is extinguished after initial ignition and the sample smokes, if the carbonization of sawdust is preceded by smoking, or if non–burned sawdust is observed inside the pile or above the locus of ignition. The burning time is measured with a stopwatch. The experiments are repeated five times, and the average time calculated over five trials is the reported burning time.

B. Test method of the sample

(a) Preparation of the sample

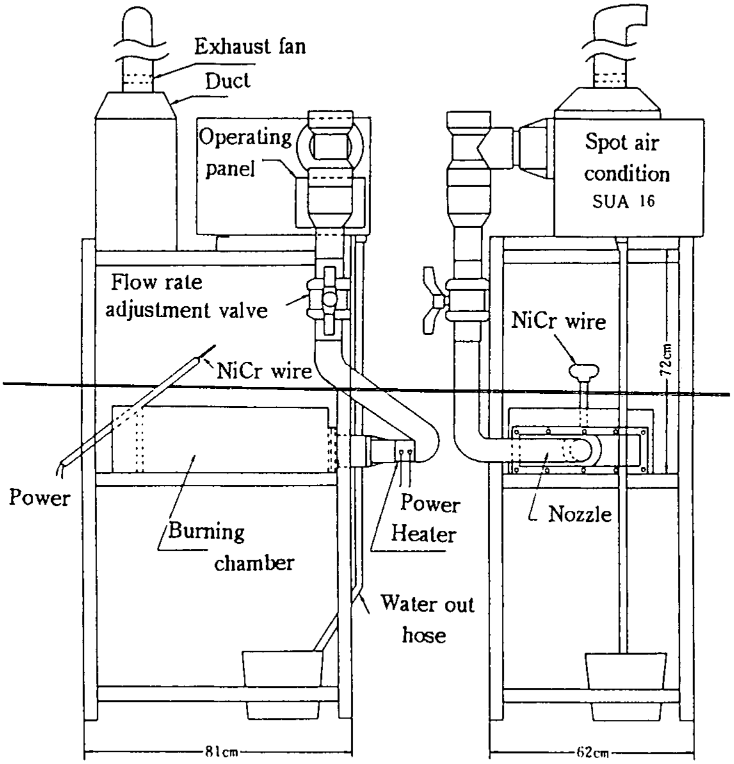
Refer to (5)A. Prepare two test samples, each having a total weight of 30 g, and one having an oxidizer: fuel ratio of 1:1, the other, 4:1 by weight. If the two samples have different burning times, the shorter time is designated as the burning time for the material being tested.

(6) Assessment of the results

The potential hazards of the the test substances are classified in the following groups: Group I is assigned to any substance of which burning time is equals to or is shorter than that of potassium bromate, or for which the burning time lies between that of potassium bromate and potassium perchlorate. Group II is assigned to any substance, the burning time of which is longer than that of potassium perchlorate.

3.5.3 The data and the property of the 30g mixture burning test

The 30g mixture burning test has been adopted by the United Nations [40] based on oxidizing burning rate tests(the 5 pound test) [39] used in America. Uehara [41] and Hasegawa [42] have concluded that this method should be adopted for the Fire Services Law in Japan. The experimental data supporting their conclusion are archived at the Hazardes Material Laboratory of Japan Carlit Co., Ltd.



Front view Side view

Figure 3.22 Combustion chamber by Uehara

A. The research by Uehara [41]

Uehara [43] has suggested the crucible method to examine the combustibility of the oxidizer–sawdust mixtures but has noted that the results may be affected by humidity. Consequently, he has built the apparatus shown in Fig. 3.22 and has achieved good reproducibility in his data. The Fire Research Institute of the Ministry of Home Affairs and the Hazardous Material Laboratory of Japan Carlit Co., Ltd. use an apparatus similar to Uehara's.

Commercially available oxidizing reagents were evaluated in the tests. Sawdust used as bedding for animals is a suitable combustible substance. A material for pets produced from boiled fish paste board and American fir tree wood called KURINCHIP, manufactured by Kurea Co. Ltd., was used in these studies. The sawdust should have a mesh size under B10.

Uehara's results from the 30 g burning test are shown in Table 3.17. A comparison of these results to the results from the 8 g burning test are shown in Fig.3.23. The good correlation between the two data sets indicates that the 8 g burning test may be used as a screening test. Uehara has recommended the 30 g burning test because it is easier to measure a burning time.

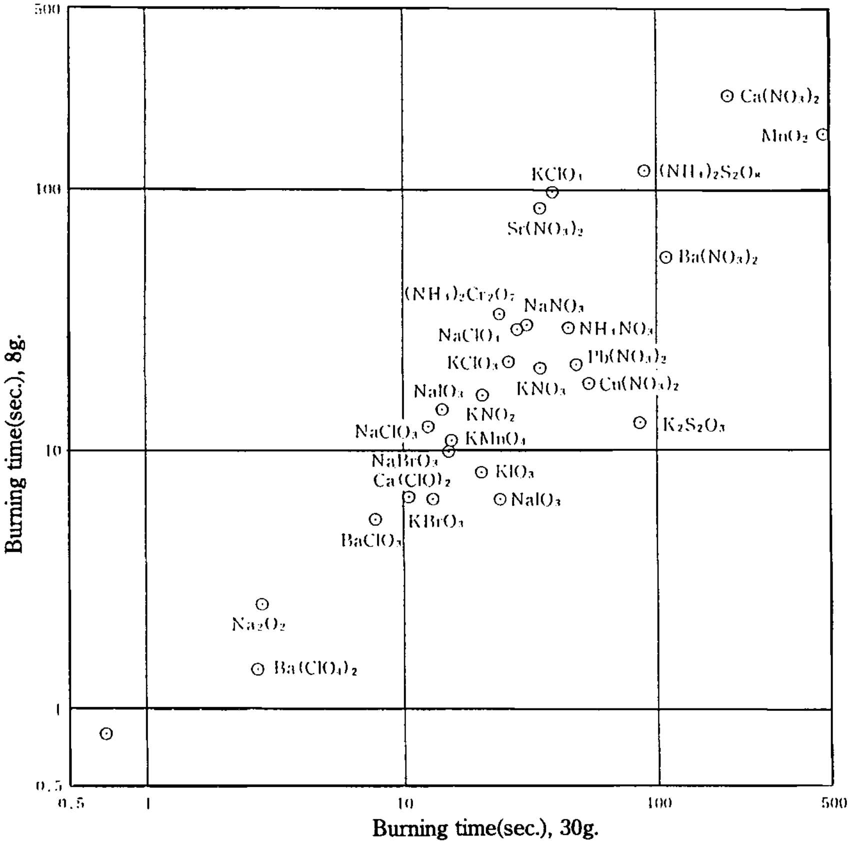


Figure 3.23 Correlation burning times of 30 g and 8 g samples

In addition, Uehara has evaluated whether a correlation exists between the burning time and the senstivity measured in the drop ball test(see Fig.3.24). The correlation coefficient between the two data sets is 0.57; therefore, Uehara suggested that both tests should be applied to evaluate hazardous materials.

The relationship between chemical composition of the oxidizer and the burning time of the sawdust has been determined by Uehara. The results are shown in Table 3.18. The trend in burning rate is tabulated as a function of the anion. The order of the burning rate of sodium salts is : chlorite > peroxide > bromate > chlorate > nitrite > iodate > perchlorate > nitrate > bichromate.

Table 3.17 Results of evaluation of oxidizers by Uehara (30g) 41)

Oxidizers	Mean time of burn (sec)		Class in Ref. 41	Class in UN 41)
	50%	80%		
$NaClO_2$	2.22	0.71	I	II
$Ba(ClO_4)_2$	19.62	2.65	I	II
Na_2O_2	6.72	2.83	I	I
$Ba(ClO_3)_2 \cdot H_2O$	35.87	7.90	I	II(*)
$NaClO_3$	11.40	11.81	I	II
$KBrO_3$	21	13	I	II
CrO_3	35.47	6.88	II	II
$Ca(ClO_2)_2(Cl>30\%)$	48.94	10.51	II	II or III
$NaNO_2$	40.80	14.67	II	III
$NaBrO_3$	30.35	15.48	II	II
$KMnO_4$	57.42	16.43	II	II
KIO_3	20.29	39.46	II	-
KNO_2	51	21	II	II
$NaIO_3$	24	25	II	-
$(NH_4)_2CrO_7$	206.85	24.31	II	II
$KClO_3$	85.91	26.03	II	II
$NaClO_4 \cdot H_2O$	148.50	28.67	II	II(*)
$NaNO_3$	67.91	30.35	II	III
$Sr(NO_3)_2$	36.50	35.15	II	III
KNO_3	52.49	35.25	II	III
$KClO_4$	188.38	38.86	II	II
NH_4NO_3	45.61	121.14	III	III
$Pb(NO_3)_2$	110.67	49.12	III	III
1,3-dibromo-5,5-dimethyl hydantoin	*98.67	51.89	III	-
$Cu(NO_3)_2 \cdot 3H_2O$	84	55	III	-
$Na_2S_2O_8$	*50.83	79.88	III	III
$K_2S_2O_4$	*38.55	85.18	III	III
$Ba(NO_3)_2$	111.70	118.52	III	II
$Ca(NO_3)_2 \cdot 4H_2O$	196.55	-	III	III(*)
MnO_2	768.28	467.06	III	-
$(NH_4)_2S_2O_8$	*89.54	*53.87	III	III

(*) Those are classified in as anhydrides in UN Orange Book,

* Part of samples were burned.

Table 3.18 Minimum burning time of salts [41] Sample mass: 8g

Substances	Ag^+	Cs^+	Li^+	Cu^{++}	K^+	NH_4^+	Na^+
Chlorite							0.79
Peroxide							2.51
Bromate					6.63		10.19
Chlorate					22.22		10.33
Nitrite					16.81		14.10
Iodate					8.33	15.86	16.36
Permanganate					10.95		
Perchlorate		10.72	2.86		98.50	3.07	29.51
Nitrate	9.88	10.78	15.87	17.90	21.12	28.49	30.11
Peroxysulfate					127.17	27.79	–
Dichromate	23.39				453.64	33.84	410.40

Substances	H	Pb	Hg	Ba	Bi	Sr	Ca
Peroxide		10.48		2.81			
Chlorate				5.35			
Hypochlorite							6.64
Iodate	36.15						
Perchlorate		3.42		1.42			24.25
Nitrate		32.85	41.89	55.18	69.33	86.33	236.62

B. Research by Hasegawa [42] and others

Hasegawa works in the Fire Research Institure of the Ministry of Home Affairs and has conducted burning tests with an apparatus as shown in Fig.3.25. He and co-workers examined factors affecting burning time. The results are shown as follows.

(1) The classification of burning conditions (refer to Fig.3.25)

The burning condition can be classified into three types.

(a) Flaming : burning with a flame.

(b) Glowing : red embers without flame are scattered and a slight burning is sustained. The surface of the embers burns.

(c) Smoldering : smoking without flame is sustained. Incomplete burning means that uncombusted sawdust results when burning is stopped halfway, and complete burning means that sawdust becomes ash or is carbonized.

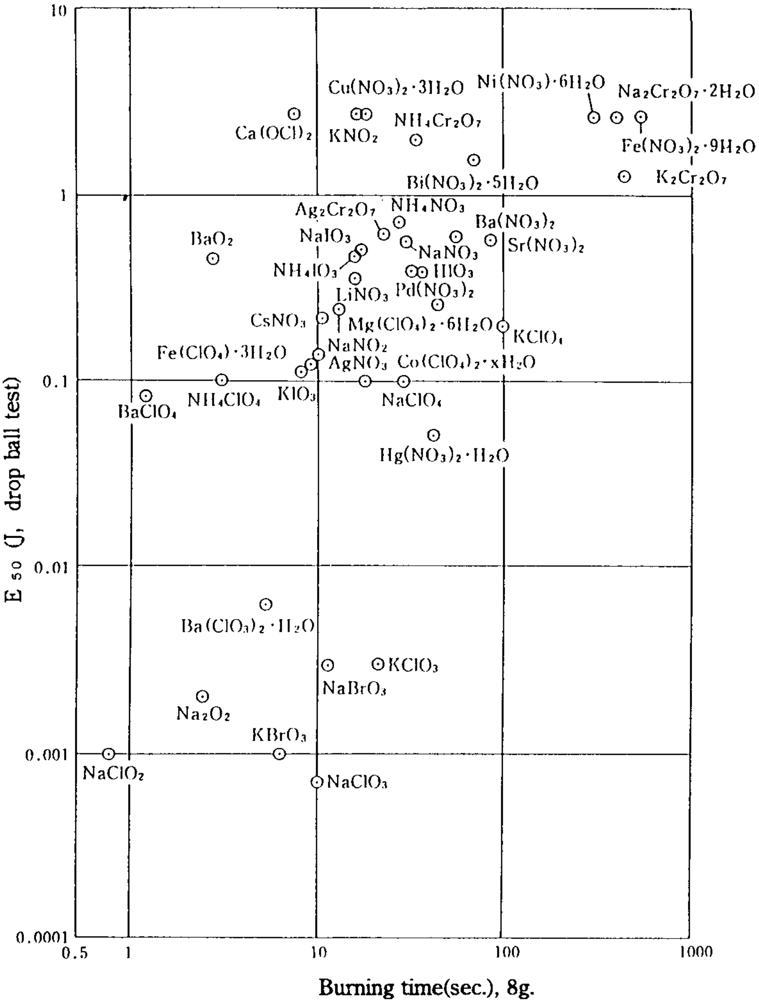
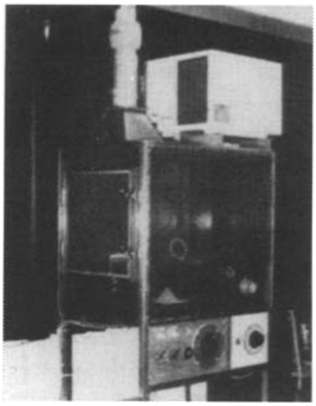


Fig. 3.24 Correlation of burning test (8g) and drop ball test

(2) The effect of the mass of the sample

The relationship between the volume of the sample and its burning time is shown in Fig.3.26. The scatter in the values of burning time becomes smaller for sample of larger mass, and the burning time per unit mass decreases with increasing sample mass and



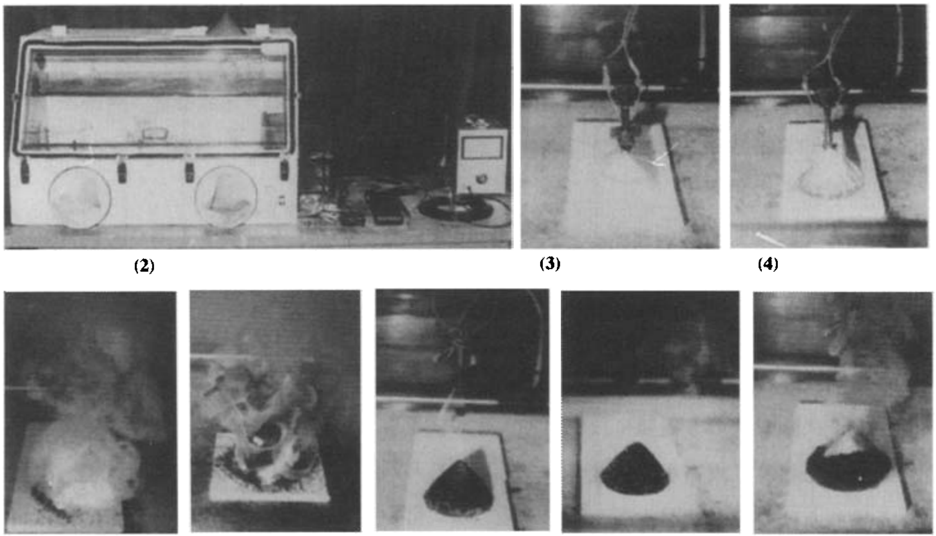
(1)

In order to determine the potential hazards of oxidizing material, a burning time of the mixtures of oxidizing materials and wood powder is measured, then is compared relativelt with each other.

(1) Combustion chamber: equipped with a ventilator for air supply and evacuation to control the temperature 20 ± 5 °C , the humidity at 50 ± 5%, and the draft velocity of air to 0.3–0.4 m/s; the chamber is at atmospheric pressure and contains an apparatus for ignition of the sample.

(2) Glove box, anemometer and hygro–thermometer: samples are weighed, mixed thoroughly at the prescribed ratio by weight of oxidizer to sawdust, and formed inside the glove box in an atmosphere dried by silica gel.

(3) Sample and igniter: the sample is formed into a conical shape on a cool, impervious, hardened ceramic plate; The igniter is Nichrome wire of 2.0 mm in diameter heated electrically to about 1000C.



(2) (3) (4)

(5) (6) (7) (8) (9)

Figure 3.25 Burning test of oxidizers

(4) At the moment of ignition: the igniter is pressed softly into the mixture until the pile ignites or until it is clear that ignition does not occur.

(5) Flaming: 30 g of a 1:1 mixture of potassium bromate and sawdust burn furiously with a flame.

(6) Flaming: 30 g of a 1:1 mixture of potassium perchlorate and sawdust burns intermittently, producing incandescent flamlets everywhere.

(7) Flaming: 15 g of pure sawdust burns quietly.

(8) Glowing: after flaming in (7), 15 g of pure sawdust burns as embers without flame and shows combustion on the surface of particles.

(9) Smouldering: 60 g of a 4:1 mixture of ammonium persulphate and sawdust smoulders while carbonization spreads gradually as a black front with smoke after flame has disappeared.

(Fire Research Institute)

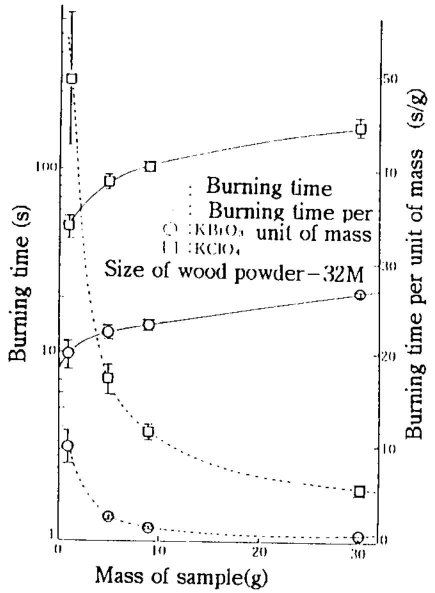


Fig.3.26 Burning time vs mass of sample [42]

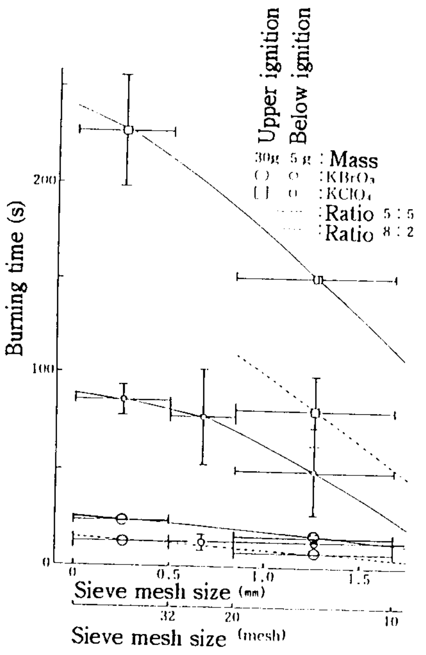


Fig.3.27 Burning time vs size of particles [42]

gradually approaches a constant value. As the mass of the sample increases, the effect of accumulating heat within the sample also increases. This is why, As has been described previously, a larger mass of sample is necessary for stable combustion. A substance with an extremely sensitive intensive burning rate, such as $KBrO_3$, may change from deflagration to detonation. For a dangerous substance, a mass of 30 g may be the limit that can be tested safely.

(3) The effect of the partical size of the sawdust

The relationship between the size of sawdust particals and burning time is shown in Fig.3.27. The larger the partical size, the shorter the burning time with either $KClO_4$ or $KBrO_3$. This trend seems independent of the ignition point, the ratio of oxidizer-sawdust mixture, and the total mass. A mixture weighing 30g with a 4:1 ratio of KClO4 to sawdust of a 32 M particle size may be ignited above the base of the pile but ceases burning and hence burns incompletely. Threrfore, a larger mesh-size of sawdust has to be used to insure sustained the burning.

(4) The effect of the locus of the ignition point

The high ignition point method requires ignition at the top of the conical pile by a coiled wire 1mm in diameter. The middle or low ignition point method calls for ignition at the surface around the circumference of the pile by a coiled wire with a diameter 2mm. The relationship

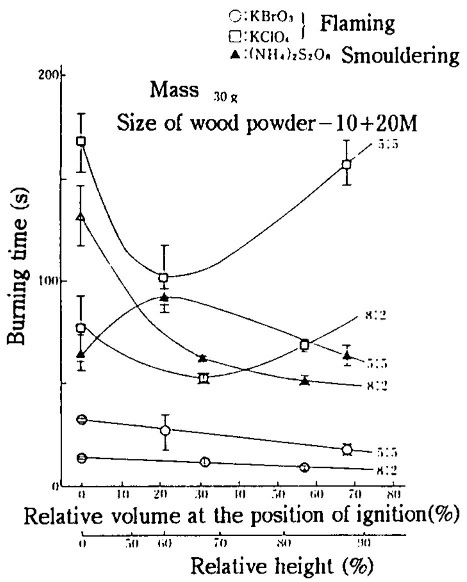


Fig.3.28 Burning time vs relative position of ignition 42)

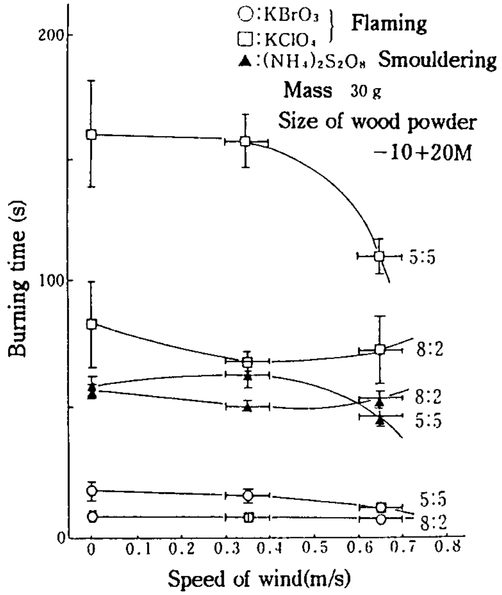


Fig.3.29 Burning time vs speed of wind 42)

between the burning time and the locus of ignition is shown in Fig.3.28. Hasegawa 42) has observed that the burning time of the KBrO$_3$ − sawdust mixture is shorter when the low ignition point method is used. The burning of the KClO$_4$ − sawdust mixture is shorter when the intermediate ignition point method is used than with either the high or low method. Even though the progress of the flame is comparatively slow, the burning rate is rapid for the middle ignition point method because the flame moves both up and down the surface of the pile simultaneously. On the other hand, the KBrO$_3$ − sawdust mixture burns more rapid when the low ignition point is used because, when the lower section of the sample is ignited, the flames heat upper part of the pile and the progression of the flames in an upward direction is accelerated. A tendency for the mixture to smolder, as happens with $(NH_4)_2S_2O_8$, is not observed as a function of the oxidizer:fuel ratio. It is, however, necessary to evaluate the data derived from the ignition point method carefully; the burning rate is more rapid and the scatter in the data is smaller when the low ignition point is used in comparison to the high point.

(5) The effect of the velocity of air currents

The relationship between the burning time

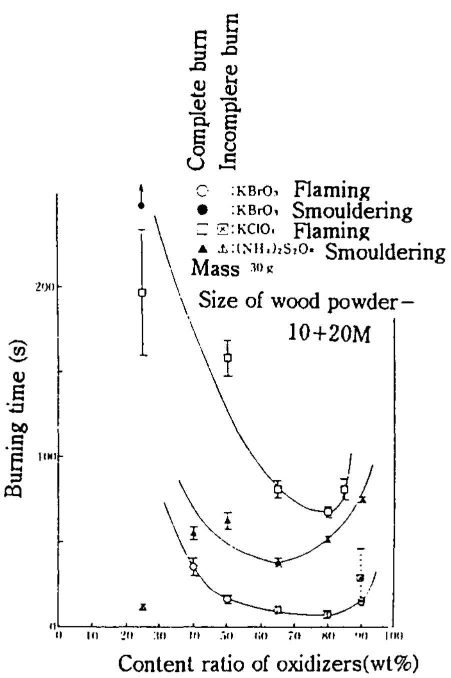


Fig.3.30 Burning time vs content ration of oxidizers [42]

and the velocity of air currents or drafts is shown in Fig.3.29. As the velocity of the air increases, the time of flaming associated with burning decreases. If the sample smolders as opposed to flames, the same trend is not necessarily found. During this test it is preferable if the velocity of any drafts is kept lower than 0.3 ~ 0.4 m/s. When no draft is present, smoke is not dispelled; therefore , a very light fraft is appropriate to enable accurate observations.

(6) The effect of changing the ratio of oxidizer to fuel

The relationship between the burning time and oxidizer contentis shown in Fig.3.30. Burning is not observed if the $KClO_4$ content is 90% by weight, if the $(NH_4)_2S_2O_8$ content is 25%, or if no oxidizer is present. The minimum value of the burning time is observed when the content of oxidizer is between 50 and 80% by weight.

3.5.4 The 500g burning test (H): The classification test for The Fire Service Law for Class 1 substances

This test is applied for substances whose particles do not pass through the 2 mm standard sieve.

(1) The purpose of the test

This test is to determine the tendency of a slid substances to increase the burning rate of a combustible substance with which it is mixed. In this test the burning time of a mixture of the material to be tested and a combustible substance is compared to a mixture of a standard and the same combustible substance.

(2) The standard substance and the combustible substance

A. The standard substance

The standard is JIS superior quality reagent potassium perchlorate of particle size between the 300 μ m (about 50 mesh) and 150 μ m (about 100 mesh). The standard is kept at least 24 hours at room temprature in a desicator containing dried silica gel.

B. The combustible substance

The combustible substance is a sawdust from a tree with a low resin level. The particle size of sawdust is between 500 μ m (about 32 mesh) and 250 μ m (about 60 mesh). The sawdust is dried at 105 ℃ for 4 hours and kept at least 24 hours at room temperature in a desicator containing dried silica gel.

(3) The test sample

The meterial to be tested is used in whatever form it is commercially produced.

(4) The site of the test

The size of the test may be either indoors or outdoors as long as there is virtually no draft.

(5) The test methods

A. The test procedure using the standard substance

(a) The preparation of the standard mixture

Mix the standard substance and the sawdust uniformly at a ratio of 2:3 by weight. The total mass of the test sample should be 500 g. The mixture is placed in a conically shaped pile on an inorganic adiabatic board at least 10 cm thick.

(b) The ignition procedure

Ignite the mixture using a fusee. Contact the base of the conical pile with the flame of the fusee until the mixture is ignited around its circumference or until it is clear that the pile does not ignite. The maximum contact time is 30 sec.

(c) Measurement of the burning time

In this test, "burning" means "flaming" and the burning time is the period from the ignition to time when the flames have dissipated. The substance is not considered to be burning if the flame goes out after ignition and the sample smokes, if the sawdust is carbonized, or if uncombusted sawdust remains inside the pile or above the site of ignition. The burning time is measured with a stopwatch. The test is carried out five times, and the reported burning time is the average of the five values.

B. The test procedure of testing a molded material

(a) The preparation of the sample for testing

Measure quantities of the test material and the sawdust at a volume ratio of 1:1; the total mass of the mixture should be 500 g. Pile the molded material in a conical shape and spread the sawdust uniformly on an inorganic adiabatic board at least 10 cm thick.

(b) The ignition procedure

Follow the procedure described in A.(b)

(c) The measurement of the burning time

Follow the procedure described in A.(c)

(6) The assessment of the results

If the burning time of the test mixture is shorter than of the standard mixture, the sample is deemed hazardous.

3.5.5 The data from the 500g burning test 45)

(1) The need for a test for molded sample

The 30g burning test for mixtures of oxidizing solids and sawdust and the drop ball impact test for mixtures of oxidizing solids and red phosphorus are used to evaluate the the burning hazards of oxidizing solids. (refer sections 3.5.2 and 3.3.7). These are appropriate tests for powdery substances which can be easily and safely handled during the experiments. These methods are not applicable to oxidizers that are produced in the molded forms.

In general the hazard decreases if a dangerous, powdery solid substance is molded into large pieces. This decrease in hazard is especially noted for solid oxidizers that become dangerous when mixed with combustible materials. A slid substance can be made safer if it is formed into larger particles. The following section describes a method for the assessment of the hazard of molded samples of solid oxiziders.

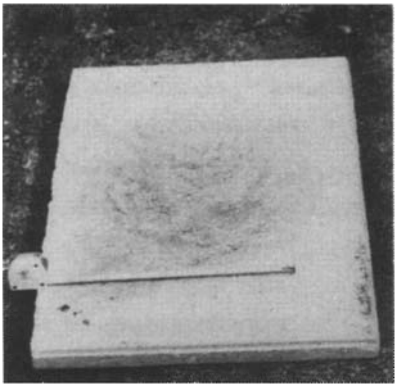
The 30g burning test is the method of choice for measuring the intensity od burniong of mixtures of powdey oxidizers and combustible materials, but this method cannot be applied to solid oxidizers that have been molded into larger shapes. The 5 lb(2, 270 g) burning rate test 39) has been proposed in the USA, but this test is on too large a scale for use in the size of apparatus available in the Japanese laboratory; hence, we did not adopt this method.

(2) The test sample

The standard oxidizing solid used in this test is a crystalline potassium perchlorate manufactured by Japan Carlit Co., Ltd. with a particle size of 60 – 150 mesh and an apparent specific gravity of 1.46 g/cm^3. The reference sample is crushed potassium perchlorate, also manufacutured by Japan Carlit Co., Ltd. with a particle size under 250 mesh and an apparent specific gravity 1.06 g/cm^3.

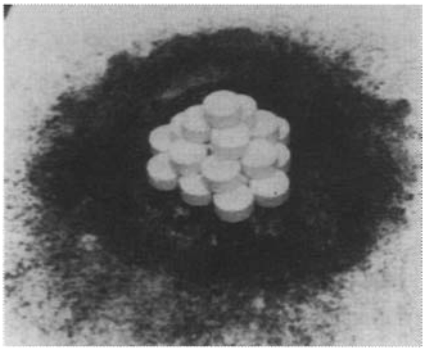
Two standard combustible materials may be used in this test. One is cellulose C, manufactured by The TOYO Filtratio Paper Co., Ltd. of particle size under 300 mesh and apparent specific gravity of 0.28 g/cm^3. The second is sawdust of 9–20 mesh in particle size with an apparennt specific gravity of 0.099 – 0.124 g/cm^3 and crushed wood for pets, made under the tradename "Woodshavings" by Japan Kurea. The sawdust is made from boiled fish paste and the board from American cedar trees. The reference sample is a fine sawdust for explosives with a particle size of 32–50 mesh and apparent specific gravity of 0.175g/cm^3 manufactured by Sanshin Industy Co., Ltd.

High strength calcium hypochlorite (HCH) molded into pieces approximately 15 mm high and 30 mm in diameter and weighing 20 g is used as the standard molded oxidizer.

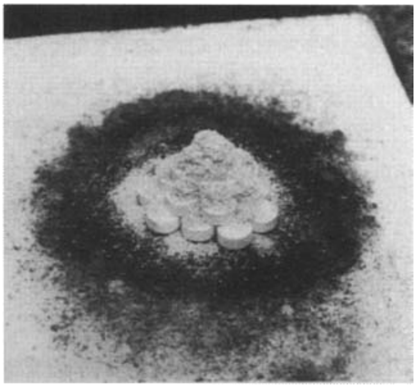


(a) $KClO_4$ –sawdust

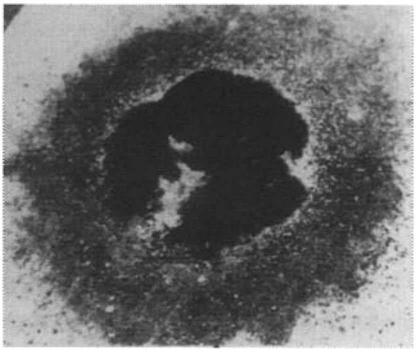
(b) Burning of $KClO_4$ –sawdust



(c) Stack of HCH pellet



(d) HCH pellet mixing with sawdust



(e) After test, no ignition

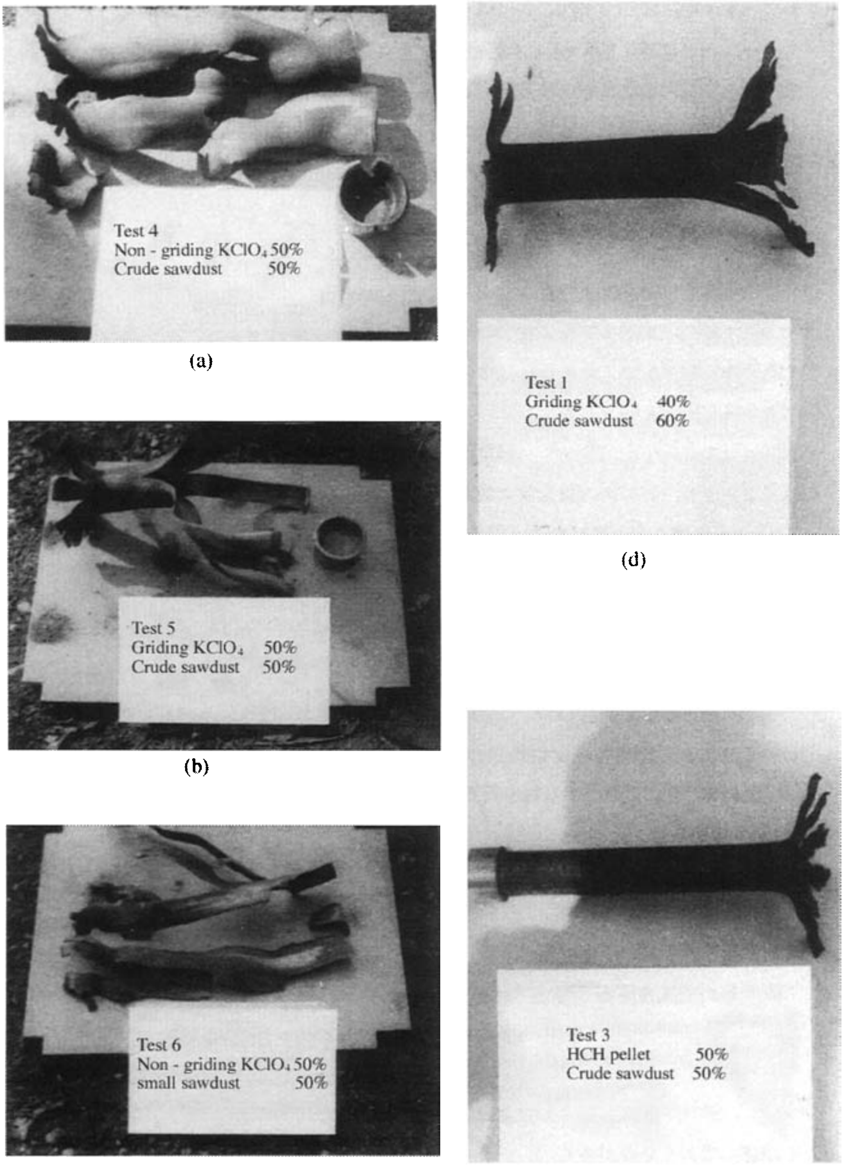
Fig. 3.31 Burning test of 500 g sample

(3) Apparatus
See Fig.3.31.

(4) The 500 g burning rate test of a mixture of standard crystalline potassium perchlorate and large−size particle of sawdust.
(a) Mix a sample of crystalline potassium perchlorate weighing 200 g with 300g of large−sized sawdust. Pile this mixture on an adiabator into a conical shape, 12 cm high and 22 cm in diameter at its base (see fig. 3.31(a)).
(b) Touch the base of the cone with the flame of an emergency fuse for motor vehicles (Hi−flare 5, manufactured by Japan Carlit Co,Ltd,.). After sufficient intensity of burning is achieved, remove the flame (Fig.3.31.(b)).
(c) Measure the time from ignition of the mixture to the cessation of burning. The end of burning is defind as the presence of a small intermittent flame; the combustion associated with this final flame is not part of the measure of burning intensity.

(5) The 500g burning rate test for a mixture of standard solid oxidizer and large−sized particles of sawdust
(a) Weight 460 g (approximately 23 pieces) of the HCH and 31 g of large−size sawdust. These masses will provide a sample with volume ratio of components of 1:1.
(b) Stack the HCH pileces in the following fashion on the adiabatic board: 12 pieces as the base, 7 pieces in the next layer, 3 in the next, and 1 on top. (Fig.3.31 (c)). Cover the stack with sawdust. The final dimensions of the conical pile are an approximately height of 8 cm and a diameter of 15 cm.
(c) Contact the base of the pile with the flame from an emergency fuse for motor vehicles. If the sample does not burn after 30 seconds of contact, remove the flame (Fig. 3.31(e)).

(6) Pre−test prior to full test: the 50/60 steel tube test
A Pre−test before a large scale test is advisable for the assessment of hazards of molded solid oxidizers. An assessment of the stability, sensitivity and ability to propagate explosion is necessary to avoid accidents at the test site. Furthermore, to carry out a lrge scale burning test safely, it is necessary to determine if a deflagration to detonation transition occurs for the standard substance.
(a) Stability
We carried out a BAM heat accumulation test on a mixture of HCH and cellulose C at a ratio of 3:1 for a period of one week at 40 ℃ . During this time, we did not observe self−accelerated heat generation. We conclced that an unexpected generation of heat does not occur during the preparation of the mixture for the 50/60 steel tube test.



(a)

(b)

(c)

(d)

(e)

Figure 3.32 The results of 50/60 steel tube of mixtures of KClO4 HCH with sawdust (in Table 3.19)

(b) The test for propagation of explosion

The possibility of a deflagration–to–detonation transition (DDT) exists if a large quantity of a self–reactive substance is burned. Non–detonatable substance do not display this hazard. The possibility of detonation can be evaluated by the 50/60 steel tube test. We have performed a 50/60 steel tube test for mixtures of crystalline potassium perchlorate and HCH with large–sized sawdust. The result are shown in Table 3.19 and Fig.3.32.

Table 3.19 Results of 50/60 Steel Tube Test of mixtures of oxidizer–combustibles

Test No.	Oxidizer (%)	Sawdust (%)	Total mass(g)	Length of tube remaining	Volume of crater	Detonation propagation
4	lg. $KClO_4$(50)	L.(50)	218	–––	356 l	Yes
5	sm. $KClO_4$(50)	L.(50)	212	10 cm	322 l	No
6	lg. $KClO_4$(50)	S.(50)	368	–––	448 l	Yes
1	lg. $KClO_4$(40)	L.(60)	258	23 cm	214 l	No
3	HCH (93.8)	L.(6.2)	786	35 cm	117 l	No

* lg.: Large particles, sm.: Small particles

In the 50/60 steel tube test, a mixture of 50% crystalline potassium perchlorate and large–size sawdust by weight demonstrated propagated of detonation (Fig.3.32(a)). When the oxidizer–fuel mixture was changed to 40% – 60%, the steel tube was not complete fractured; approximately 23 cm of the tube remained intact. It is conceivable that the potassium perchlorate separates from the sawdust and settles to the bottom of the tube when the mixture is poured. The tube may then be split in the region opposite the initiator where the oxidizer concentration is highest. In light of this observation, a ratio of crystalline potassium perchlorate to sawdust of 40%:60% by weight is used for the standard in the 500 g burning rate test. As a reslt of the primary test, the standard mixture of HCH and large–sized sawdust for the burning rate test should be a 1:1 mixture by volume. The spceific gravity of samples of small–sized sawdust is so small compared to the molded HCH, a 2:3 ratio by weight results in the majority of the test sample being composed of powdery sawdust. Because the mixture of HCH and sawdust at a ratio of 1:1 by volume does not detonate in the 50/60 steel tube test, we decided it was safe to carry out the 500 g burning ate test.

(7) The result of the primary test

(a) The burning rate of the standard

The results of the burning rate test performed on the standard mixture of crystalline potassium phosphate and particles of large–sized sawdust are shown in Table 3.20. A pile of a 40%:60% mixture by weight of the oxidizer and fuel burns itself out in about 150 sec. after being ignited at the base by the flame of an emergency fuse. If the ignition is insufficient, the flame does not spread initially and burning is prolonged.

(b) The tendency of the HCH mixture to burn

A conical pile with a total mass of 500 g consisting of a 1:1 mixture by volume of HCH pieces and large–sized sawdust at (which corresponds to 93.8% by weight HCH) did not ignite when contacted by a fuse for more than one minute. In comparison to a mixture containing powdery potassium perchlorate, this mixture does not have a tendency to accelerate burning.

Table 3.20 Results of the burning test on 500 g of mixtures of oxidizers and sawdust

Test No.	Oxidizers (%)	Total mass (g)	Burning time (sec)
1	lg. particle $KClO_4$(50)	226	224
2	lg. particle $KClO_4$(40)	226	194
3	lg. particle $KClO_4$(40)	500	143
4	lg. particle $KClO_4$(40)	500	259
5	lg. particle $KClO_4$(40)	500	165
6	HCH (93.8)	500	No ignition

3.5.6 Deflagration test (I)

U.N. Classification test for organic peroxides (C.2) 37)

I.1. Property tested

Violence of deflagration

Deflagration, is the subsonic propagation of a reaction front through the organic peroxide without the participation of oxygen from the air.

I.2. Apparatus and materials

The test is performed with a Dewar vessel (see Fig.3.33) provided with vertical observation windows at opposite sides. A timer with an accuracy of 1 second is used to measure the deflagration rate.

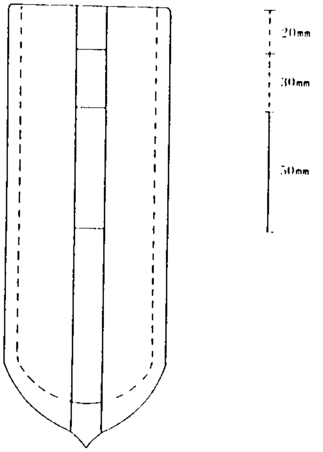


Fig. 3. 33 Dewar vessel with seeing-window used in deflagration test

The Dewar has a volume of about 300 cm ^{3}, has an internal diameter of 48 ± 1 mm, an external diameter of 60 mm and a length between 180 and 200 mm. The half-time of cooling with 265 cm ^{3} of water in the Dewar, closed by a cork, should be longer than 5 hours. Horizontal graduation marks are drawn at 50 and 100 mm from the top of the Dewar. The time it takes for the decomposition front to propagate from the 50 mm mark to the 100 mm mark yields the deflagration rate. A glass thermometer with an accuracy of 0.1 is used to measure the temperature of the test substance prior to ignition.

Any gas flame with a flame length of at least 20 mm can be used to ignite the substance. For safety reasons it is necessary to perform exploratory tests in glass-pyrex-tubes prior to the Dewar test. The diameter of the glass tube should be significantly smaller than that of the Dewar vessel. It is recommended to perform the test in a 14 mm diameter tube first and subsequently a test in a 28 mm diameter tube. If the deflagration rate in any of these exploratory tests exceeds the value of 5 mm/s, the substance can be classified as a fast deflagrating substance and the main test can be omitted for the sake of safety.

For personal protection the test is performed in an explosion-proof fume-chamber or in a well-ventilated test-cell. The capacity of the exhaust fan should be large enough to dilute the decomposition products to the extent that no explosive mixtures with air can be obtained. A stable, shatter-proof glass shield must be placed between the observer and the Dewar.

I.3. Test

The Dewar vessel as well as the substance are brought to the emergency temperature as defined in the Recommendations. If the substance is sufficiently stable as to require no emergency temperature, a test temperature of 50 ℃ is to be used. The Dewar is filled with 265 cm ^{3} of the organic peroxide. Granular substances are filled into the Dewar in such a way that the bulk density of the substance is comparable with that in practical situations. Liquids are poured into the glass tube.

Pasty materials are introduced into the vessel in such a way that no air pockets were present in the sample. The height of filling should be about 20 mm below the rim of the vessel. The weight and the temperature of the substance are recorded. The vessel is placed in the test-cell or fume-chamber behind the glass shield, after which the substance is heated at the top by means of a gas burner. Once ignition has been observed or, alternatively, once it is clear that ignition will not occur, the gas burner is removed and extinguished. The period of time required for the reaction zone to pass the distance between the two marks is measured with the timer. If the reaction stops before reaching the lower mark, the substance is considered to be non−deflagrative. The test is performed in duplicate and the shortest time interval is used for the calculation of the deflagration rate.

I.4. Assessing results

The participation of oxygen from the air in the reaction at the sample surface is negligible after the reaction zone has propagated over a distance of 30 mm. Therefore the reaction zone will extinguish if the substance does not deflagrate under the test conditions. If, on the other hand, the substance can deflagrate, the reaction zone will continue to propagate downwards through the substance. The propagation velocity of the reaction zone (deflagration rate) is a measure of the susceptibility of the substance to deflagration under atmospheric pressure.

I.5. Test criteria

Rapid propagation: The deflagration rate is greater than 5.0 mm/s.

Slow propagation : The deflagration rate is less than or equal to 5.0 mm/s and greater than or equal to 0.35 mm/s.

No propagation : The deflagration rate is less than 0.35 mm/s.

Note : The time/pressure test, test C.1, is to be carried out if rapid propagation is not obtained.

& 1. Potassium Perchrolate Reagent (JIS K 8226−1986)
& 2. Rim of Japan cedar
& 3. Thermal conductivity of original check board is 0.1 W/(m.K)
& 4. Ratio of height and radius of conical pile is 1:2.
& 5. Prescribed in emergency fuse for motor vehicles(JIS D 5711−1982)
& 6.

Table 3.21 Examples of results of UN Deflagration Test(C.2)

Substance	UN No.	Sample mass (g)	Test temp. (℃)	Rate (mm/s)	Result
Dibenzoyl peroxide, technically pure	2085	158	20	100 a)	Yes, rapidly
tert−Butyl peroxybenzoate, technically pure	2097	276	50	0.65	Yes, slowly
Di−tert butyl peroxide, technically pure	2102	212	50	0.27	No
tert−butyl peroxy−3,5,5−trimethylhexanoate, 75% in solvent	2104 b)	238	50	0.27	No
Cumyl hydroperoxide, 80% with cumene	2116 b)	273	50	0.12	No
Dicumyl peroxide, technically pure	2121	292	50	No ignition	No
Dilauroyl peroxide, technically pure	2124	130	45	No ignition	No
tert−Butyl peroxy−2−ethylhexanoate, technically pure	2143	237	25	0.74	Yes, slowly
Dicyclohexyl peroxydicarbonate, technically pure	2152	−	26	26	Yes, rapidly
Dicyclohexyl peroxydicarbonate, 90% with water	2153	−	15	13	Yes, rapidly
Di−(4−tert−butylcyclohexyl) peroxydicarbonate, technically pure	2154	123	35	4.3	Yes, slowly
2,5−Dimethyl−2,5−di−(tert−butylperoxy) hexyne−3, technically pure	2158	235	50	2.9	Yes, slowly
Dicetyl peroxydicarbonate, technically pure	2164	159	35	No ignition	Yes, slowly
2,5−Dimethyl−2,5−di−(benzoylperoxy) hexane, technically pure	2172	231	50	6.9	Yes, rapidly
Dilauroy peroxide, 42% stable dispersion in water	2893	265	45	No ignition	No

a) Performed with an exploratory test using a glass tube with a diameter of 14 mm at 20 ℃ instead of 50 ℃.

b) UN number refers to the technically pure product.

3.5.7 UN time/pressure test(J) : UN test for organic−peroxide classification

J.1 Property to be used: Deflagration rate a) . (See 3.5.6)

J.2 Apparatus and Materials

J.2.1 The time/pressure apparatus (Fig.3.34) consists of a cylindrical steel pressure vessel 89mm in length and 60mm in external diameter. Two flats are machined on opposite sides (reducing the cross-section of the vessel to 50mm) to facilitate holding while fitting the firing plug and vent plug. The vessel, which has a bore 20mm diameter, is internally rebated at either end to a depth of 19mm and threaded to accept 1"BS ϕ . A pressure take-off, in the form of a side-arm, is screwed into the curved face of the pressure vessel 35mm from one end and at an angle of 90 degrees to the machined flats. The sockets for this are bored to a depth of 12cm and threaded to accept the 1/2" BS ϕ thread on the end of the side-arm. A copper washer is fitted to ensure a gas-tight seal. The side-arm extends 55mm beyond the body of the pressure vessel and has a bore of 6mm. The end of the side-arm is rebated and threaded to accept a diaphragm-type pressure transducer. Any pressure measuring device may be used provided it is not affected by hot gases or decomposition products and is capable of responding to a rate of pressure increase of 690-2070kPa (100-300 psig) in under 5ms.

J.2.2 The end of the pressure vessel furthest from the side-arm is closed with a firing plug which is fitted with two electrodes, one insulated from and the other grounded to the plug body. The other end of the pressure vessel is closed with an aluminium rupture disk 0.2mm thick (bursting pressure approximately 2200 kPa (320 psi)) held in place with a retaining plug which has a 20 mm bore. A soft lead washer is used with both plugs to ensure a good seal. A support stand (Fig.3.34 bottom) holds the assembly at the correct angle during use. This consists of a soft steel base plate measuring 235mm x 6mm x 185mm and a long square hollow section 70mm x 70mm x 4mm.

J.2.3 A section is cut from each of two opposite sides at one end of the length of the square hollow section so that a structure having two flat sided legs surmounted by an 86mm length of intact box results. The end of each flat side is cut at an angle of 60 degrees to the horizontal and welded to the base plate.

J.2.4 A slot measuring 22mm wide x 46mm deep is machined in one side of both the upper section and the base section such that when the pressure vessel assembly is lowered, firing plug end first, into the box support, the side-arm is accommodated in this slot. Packing pieces of steel 30mm wide and 6mm thick are welded to the lower

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Note a) The time/pressure test has been designed to examine the effect of an ignition on substances under confinement and, in particular, the possibility that ignition might lead to a deflagration with explosive violence at pressures which can be attained by substances in normal commercial packages.

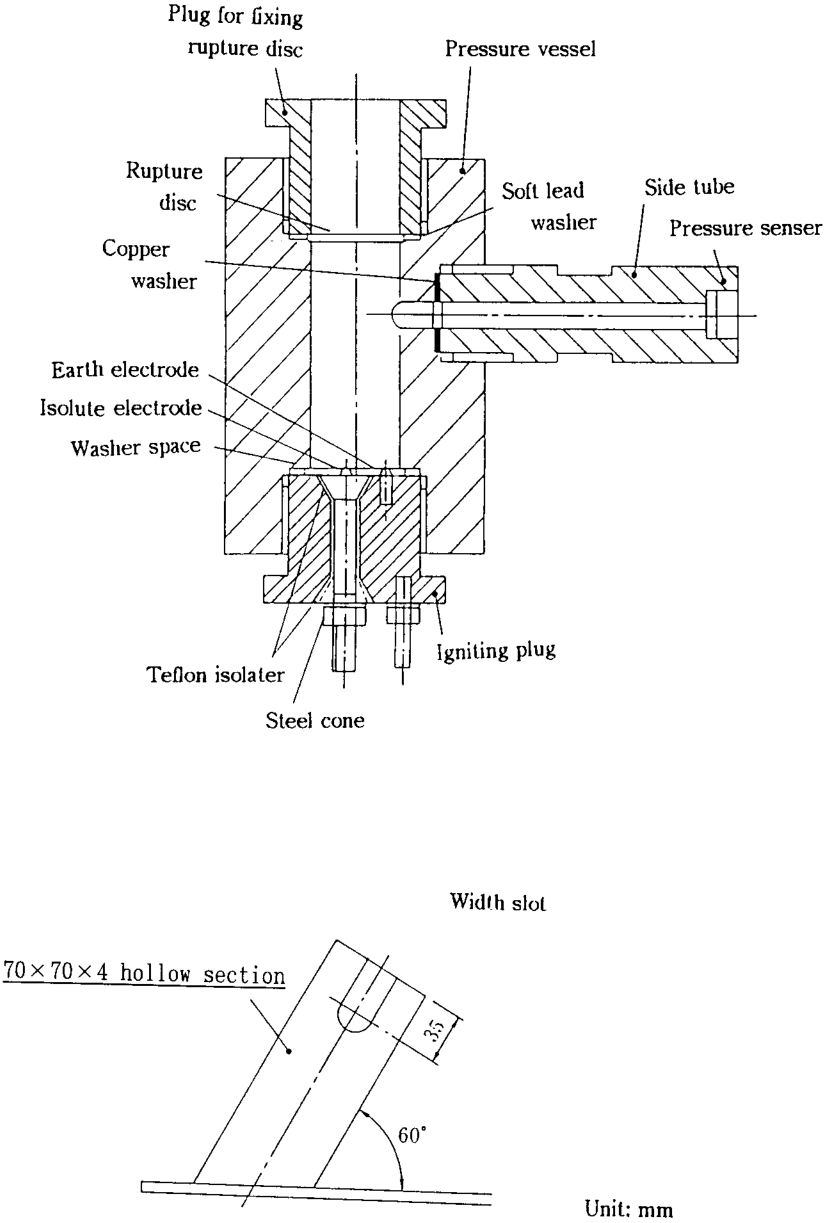
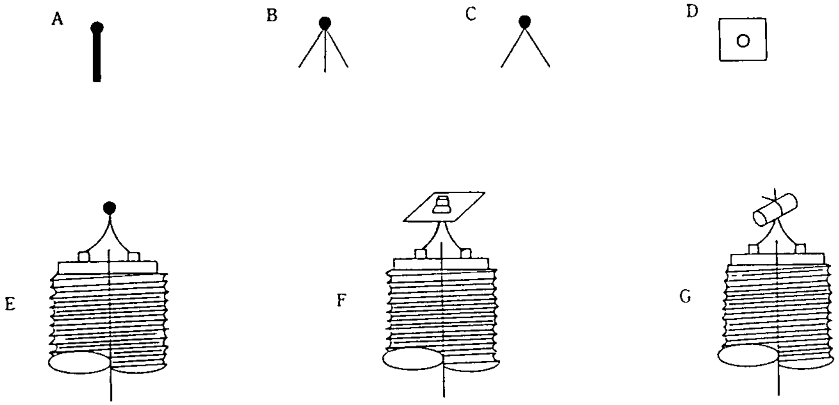


Figure 3.34 Installation (upper) and support (below9 of time/pressure test (C,1)

internal face of the box to act as spacers. Two 7mm thumb screws taped into the opposite face hold the pressure vessel firmly in place. Two 12mm wide strips of 6mm thick steel welded to the side pieces abutting the base of the box support the pressure vessel from beneath.



A Electric fusehead in time of manufacture
B Brass foil contact from card isoluter
C Cut from isolute card
D Linen fabric SR525 coated with igniter
E Fusehead in igniting plug
F Linen fabric on the fuse head
G Linen fabric which was well set

Fig. 3.35 Igniting system of time/pressure test (C, 1) used for solids

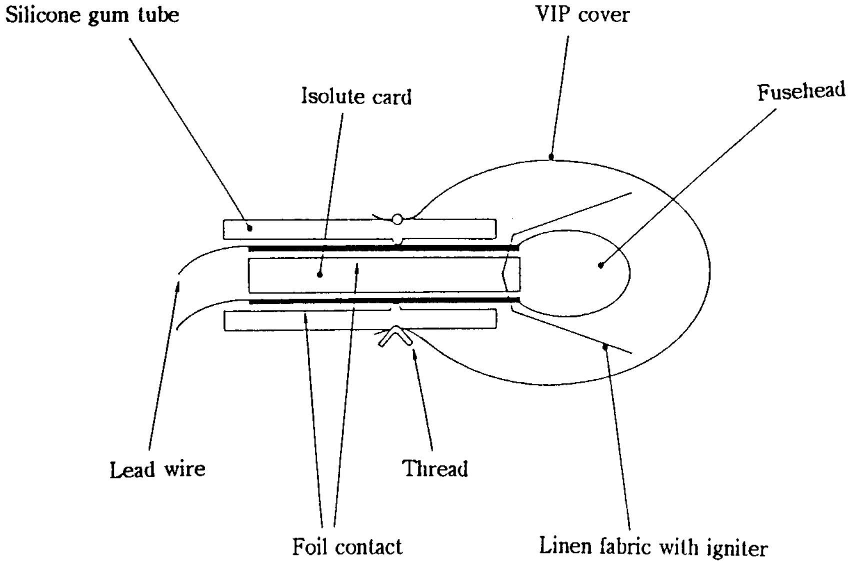


Fig. 3.36 Igniting system of time/pressure test (C, 1) used for liquids

J.2.5 The ignition system is composed of an electric fusehead of the type commonly used in low pressure detonators, together with a 13mm square piece of primed cambric. Other fuseheads with equivalent properties may be used.

J.2.6 Primed cambric is a linen fabric coated on both sides with a potassium nitrate/silicon/sulfurless gunpowder pyrotechnic composition [a)]. The procedure for the preparation of the ignition assembly for solids starts with separation of the brass foil contacts of an electric fusehead from its insulator (See Fig.3.35). The exposed portion of the card is then cut off. The fusehead is then soldered onto the terminals of the firing plug by means of the brass contacts such that the tip of the fusehead is 13mm above the surface of the firing plug. A 13mm square piece of primed cambric is pierced through the center and positioned over the attached fusehead, around which it is then folded and secured with fine cotton thread.

Note a) Obtainable from HSE, and FEL3C in UK.

J.2.7 For liquid samples, leads are soldered onto the contact foils of the fusehead. The leads are then threaded through an 8mm length of 5mm o.d. and 1mm i.d. silicone rubber tubing, and the tubing is pushed over the fusehead contact foils as shown in Fig.3.36. The primed cambric is then wrapped around the fusehead and a single piece of thin PVC sheathing, or its equivalent, is used to cover the primed cambric and the silicone rubber tubing. The leads are then soldered onto the terminals of the firing plug such that the tip of the fusehead is a 13mm above the surface of the firing plug.

J.3 Procedure

J.3.1 The apparatus is assembled, complete with pressure transducer but without the aluminium rupture disk, end down in a supported firing plug. Five grams of the test substance are introduced into the apparatus in contact with the ignition system.Normally no tamping is carried out when filling the apparatus unless it is necessary to use light tamping to get the 5g charge into the vessel. If, even with light tamping, it is imposible to fill the vessel to capacity, the weight of the charge used should be noted. The lead washer and aluminium rupture disk are placed in position and the retaining plug is screwed in tightly. The charged vessel is transferred to the firing support stand, rupture disk uppermost, which should be contained in a suitable, armored fume hood. An exploder dynamo is connected to the external terminals of the firing plug and the charge is fired. The signal produced by the pressure transducer is recorded on a suitable system which allows both an evaluation and a permanent record of the time/pressure profile to be recorded (e.g. a transient recorder coupled to a chart-recorder).

J.3.2 The test is carried out three times. The time taken for the pressure to rise from

690 kPa (100 psig) to 2,070 kPa (300 psig) above atmospheric pressure is noted. The shortest time interval shall be used to determine the classification.

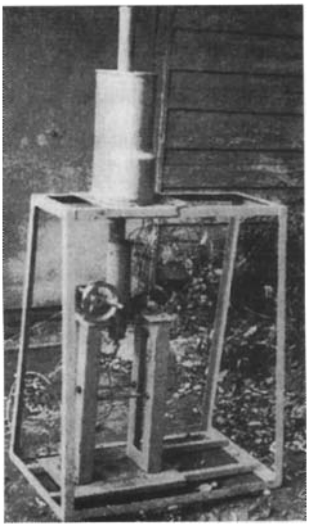


Fig. 3.37 Photo of modified time/pressure test instation

J.4 Assessing results

The substance is considered to present an explosion hazard by deflagration if the time interval is less than 30ms in any one test.

J.5 Test criteria

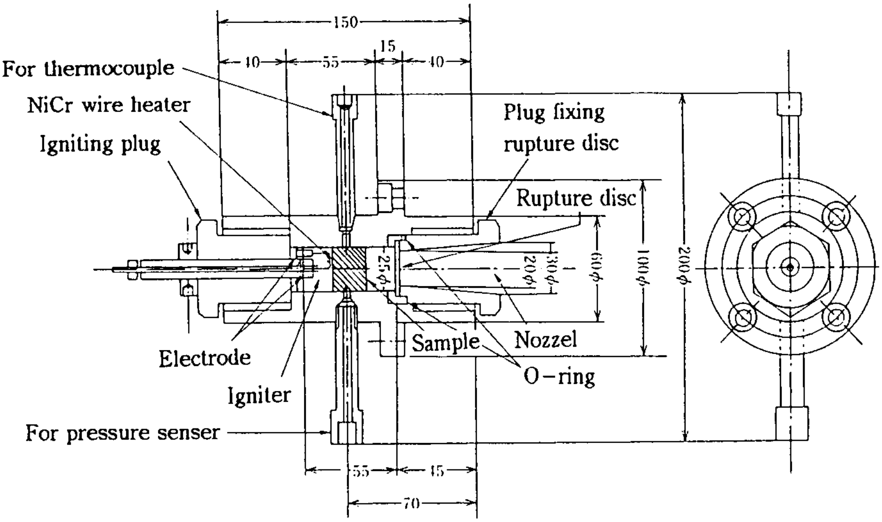


Fig. 3.38 Illustration of modified time/pressure test installation

"Yes, rapidly" : – The time for pressure rise from 690 kPa to 2070 kPa is less than 30 ms.

"Yes, slowly" : – The time for pressure rise from 690 kPa to 2,070 kPa is equal to or greater than 30 ms.

"No" : – The pressure rise to 2070 kPa above atmospheric pressure is not achieved.

Note : The deflagration test, Test C.2, is to be carried out to distinguish between "Yes, slowly" and "No", if necessary.

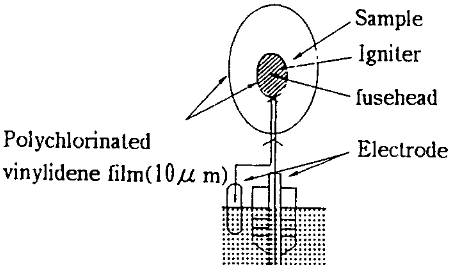


Fig. 3.39 Igniting part used for liquid samples

J.6 Test results(example)

Examples of the test results are shown in Table 3.22.

3.5.8 Improved time/pressure test (K)

K.1 Property to be tested 81, 82)

Deflagration rate a) (See 3.5.6)

K.2 Test apparatus 81 – 83)

The test apparatus as shown in Fig.3.37 – 3.40 consists of a combustion chamber, a firing system and a data acquisition system.

(1) Combustion chamber

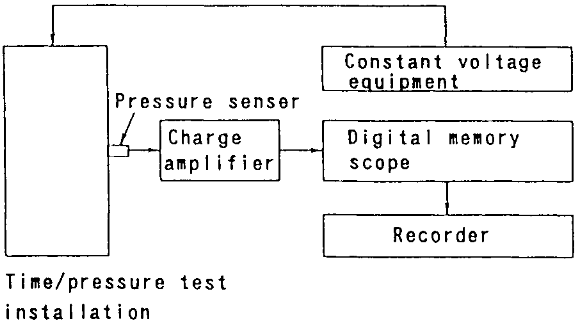


Fig. 3.40 Measuring equipment of modified time/pressure test

The combustion chamber is made out of a steel cylinder (60mm o.d.x 89mm in length) with two steel plugs screwed in at both ends (internal volume 27cm ^{3}). At the plug at the lower end there are two electrodes either for a Nichrome wire heater (0.05mm o.d. x 100mm length)or a fusehead, and at the upper end a set of rupture disks with a pressure rating of 2,070 kPa or higher (e.g. a 0.15 mm thick brass sheet disk having a rating of 1,000 kPa may be used) is installed. At the side of the cylinder are two nozzles made out of steel pipe that face each other and are screwed perpendicularly to the cylinder body for measuring the pressure change due to the deflagration during testing.

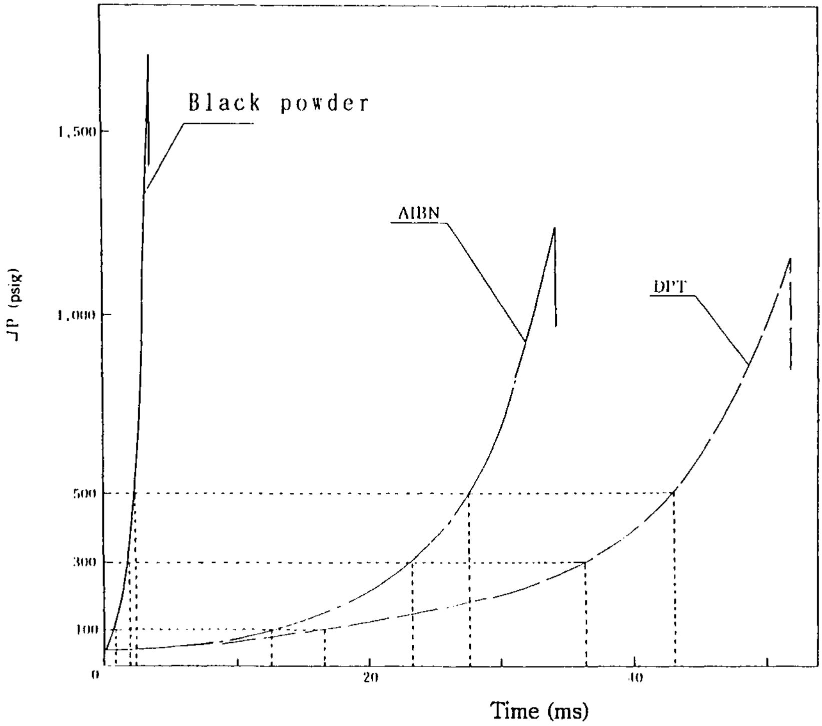


Fig. 3. 41 Characteristic increasing pressures by typical reactive substances in the improved time/pressure test

Sample quantity : 5g

Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g

Method of ignition : Nichrome wire at bottom

(2) Firing system

The firing system consists of an igniter that sets fire to the sample to be tested, two electrodes that have either a Nichrome wire heater or a fusehead that initiates a fire at the igniter, and a 12V constant volt electric source that supplies electricity to the system.

(3) Data acquisition system

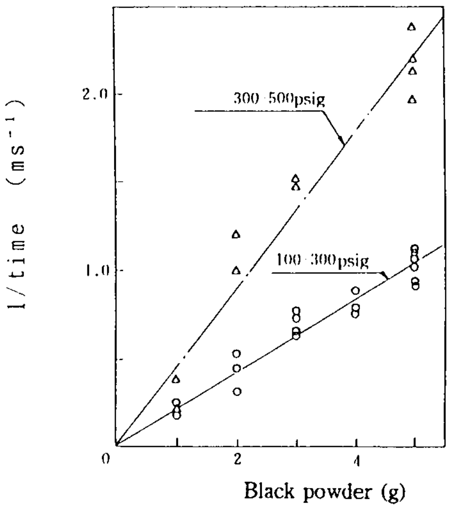


Fig. 3. 42 Relationship between rate of increasing pressure and amount of sample (gunpowder) at deflagration in the improved time /pressure test
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

The data acquisition system consists of a pressure sensor attached to a nozzle on the side of the cylinder body (the sensor should not be affected by the hot gases or decomposition products and should be capable of responding to a rate of pressure increase between 690 kPa (100 psig) and 2,070 kPa (300 psig) within 5ms), an amplifier for signals from the sensor, and a digital memory scope that has a recording system; the system should correspond to the input described above.

K.3 Test procedure 81-83)

(1) Preparation of igniter, composed of minium (70wt.%) and silicon (30wt.%), for about 1 to 5g as is required.

(2) Preparation of the sample to be tested, as much as 5g.

(3) The pressure probe with the sensor is attached to the testing device, and the lead wires are connected to the recorder.

(4) In the case of solid sample, a Nichrome wire heater as a firing igniter is connected to the electrodes on a plug, which is then screwed to the lower end of the pressure vessel body.

The igniter (1 g) is charged evenly over the heater through the opening in the upper end of the vessel body, after which 5g of the sample is loaded evenly at the bottom of the combustion chamber.

In the case of a liquid sample, 1g of the igniter is enclosed within a sheathing which will not affect the burning rate of the sample (e.g., 10 μ m thick PVC film), and a fusehead is set at the center of this ignition system. The ignition system is placed in the middle of the liquid sample which is enclosed in the same PVC sheathing. To prevent the sample from leaking out of the sheathing, the end of the film pack is tightened by a thread around the neck of the pack. The lead wires of the fusehead are connected to the terminals on the plug.

(5) The rupture disk described above is seated at the bottom of the opening at the upper end of the cylinder. Over the disk, the retaining plug is screwed tightly down so that the disk is securely placed in the correct position; an O–ring is used to seal it.

(6) The retaining plug holding the rupture disk is connected to a silencer situated above the test rig.

Table 3.22 Examples of results of Time/Pressure Test(C.1)

Substance	UN No.	Time(ms)	Result
Dibenzoyl peroxide, technically pure	2085	1	Rapidly propagating
Dibenzoyl peroxide, 75% with water	2090	20	Rapidly propagating
tert-Butyl hydroperoxide, 70% with water	2093	Max.1380kPa	No propagation
tert-Butyl peroxybenzoate, technically pure	2097	2500	slowly propagating
Di-tert butyl peroxide, technically pure	2102	100	slowly propagating
Cumyl hydroperoxide, 80% with cumene	2116 [a)]	No ingition	No propagation
Dicumyl peroxide, technically pure	2121	No ignition	No propagation
Dicumyl peroxide, with 60% inert solid	2121 [b)]	No ignition	No propagation
Dilauroyl peroxide, technically pure	2124	900kPa400 at 400ms	slowly propagating
tert-Butyl peroxy-2-ethylhexanoate, technically pure	2143	4000	slowly propagating
2,5-Dimethyl-2,5-di-(tert-butylperoxy) hexyne-3, technically pure	2158	70	solwly propagating
Dicetyl peroxydicarbonate, technically pure	2164	No ignition	No propagation
Magnesium monoperoxyphthalate hexahydrate, 85% with magnesium phthalate	----	Max.900kpa	No propagation

a) UN number refers to the technically pure product.

b) See "Special Determination" No.73

(7) All the wiring is done to form a circuit. The switch in the circuit is closed so that electricity flows from the constant voltage power supply. All of these things are done after confirmation is received that people have evacuated the testing site.

(8) Any changes of pressure over time caused by deflagration of the sample are recorded. The deflagration is initiated by a flame from the igniter fired by the fusehead or the Nichrome wire heater and occurs under conditions of a confined sample. The time it takes the pressure to rise from 690kPa (100psig) to 2,070kPa (300psig) is recorded (now defined as "time interval").

(9) The same test is conducted three times, and an average time is noted.

(10) The igniter charged for the initial test is 1g and is increased up to 5g in 1g increments to find the minimum value of the time interval. The tests are conducted three times at each level of charge.

(11) The times of increasing pressure caused by deflagration under conditions of sample confinment and the average values for the tests are noted together with the amount of igniter used for each test.

K.4 Assessing results

The tested sample is said to present an explosion hazard by deflagration if the time required for the pressure to increase from 690kPa (100psig) to 2,070kPa (300psig) is less than 30ms.

K.5 Test criteria

The time interval required for the pressure to increase from 690kPa (100psig) to 2,070kPa (300psig) is the criterion.
"Rapid propagation" : The time interval is less than 30ms.
"Slow propagation" : The time interval is greater than or equal to 30ms.
"No propagation" : The pressure does not increase to 2,070kPa (300psig) above atmospheric pressure.

Note : If necessary, the deflagration test (C2) may be carried out to distinguish between "Slow" and "No propagation".

K.6 Features of improved type time/pressure test [81, 82]

The comparison of the improved time/pressure test method with the test by HSE [52, 84] reveals that the inner volume of the pressure vessel is larger by as much as 27cm^3 (20cm^3 for HSE); it has a branch nozzle for temperature measurement on the vessel body; it can be rotated to a position at any angle, and it has a silencer located at the testing rig. No essential difference exists between the two methods. However, there is a difference in the method of ignition.

The HSE method uses a primed cambric of 13mm x 13mm coated with a potassium nitrate/silicon propellant ignited with a match; the propellant has a caloric value of 3.3 – 3.8 J/g, and the prime cambric of the size 13mm x 50mm requires 40 to 45ms for the pressure to increase from 690kPa (100psig) to 2,070kPa (300psig). The combustion of the igniter itself provides some increase in the pressure in the HSE method, whereas the igniter in the improved method is not responsible for an increase in pressure. Therefore, one measures a true pressure increase caused solely by the deflagration of the test sample. Another difference is in the rupture disk. The one used in the HSE method is an aluminum sheet 0.2mm thick with a pressure rating of 2,070–2,208kPa(300–320psig) that tends to leak combustion gases when it is subjected to heat and that has a lower pressure rating. The improved method uses mainly a brass sheet 0.15mm thick that improves upon all of these points.

K.7 Test results(example)

K.7.1 Some considerations about standard test conditions [81, 82]

(1)Curves of increasing pressure from the standard testing method

Fig.3.41 shows typical increasing pressure curves generated by deflagration of the standard test samples using 5g of gun powder, AIBN, or DPT respectively, which is loaded over the 1g minium(Pb_3O_4)/silicon type igniter (minium : 70wt.%, silicon : 30wt.%). The rupture disk used is a brass sheet 0.15mm thick. Since there is no increase in pressure due to the combustion of the igniter, pressure increases shown are considered purely due to the deflagration of the test samples. As shown, the pressure increase continues to accelerate as the deflagration progresses and finally reaches a point where the rupture disk bursts. The rate of pressure increase varies with the kind of reactive chemical tested. The rates are shown in order: DPT < AIBN < gunpowder. This method, therefore, can be used to assess the deflagration rate of reactive chemicals.

Table 3.23 The effect of ignition methods on deflagration of reactive chemicals using modified time/pressure test

Substances	Ignitor Pb_3O_4 (wt.%)	Si (wt.%)	(g)	Ignition method	Onset time of pressure (ms) 100-300psig	300-500psig
--	70	30	1	NC,B	No propagation	
	70	30	2	NC,B	No propagation	
	70	30	5	NC,B	No propagation	
Black powder	--		1	NC,B	0.71	0.45
	70	30	1	NC,B	0.95	0.45
					0.92	0.45
	70	30	1	NC,U	1.03	0.49
	70	30	1	FH,C	1.24	0.52
					1.16	0.45
AIBN	--			NC,B	10.9	4.0
	90	10	1	NC,B	9.8	3.3
					8.4	2.8
	70	30	1	NC,B	11.1	3.7
	50	50	1	NC,B	6.2	4.7
	70	30	0.5	NC,B	10.4	3.0
	70	30	1.5	NC,B	10.2	3.9
	70	30	1	NC,U	11.6	4.1
DPT	--			NC,B	24.9	7.5
	70	30	1	NC,B	19.0	7.6
					22.3	7.1
	70	30	5	NC,B	23.7	8.0
	70	30	1	NC,U	29.3	7.6
					23.7	8.5

Rupture disk:copper, thickness 0.15mm,
NC,B: Nichrome wire heater, ignition from below,
NC,U: Nichrome wire heater, ignition from top,
FH,C: Fusehead, ignition from center.

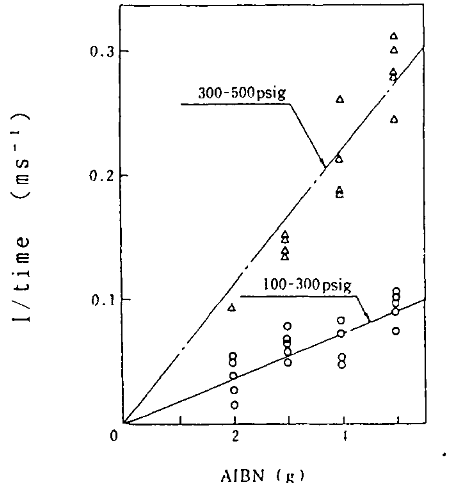


Fig. 3. 43 Relationship between rate of pressure increase and amount of sample (AIBN) at deflagration in the improved time/ pressure test
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

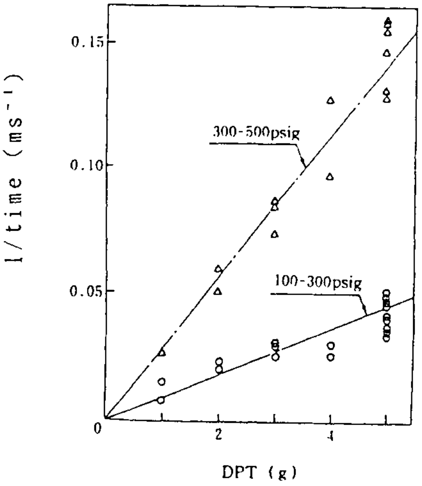


Fig. 3. 44 Relationship between rate of pressure increase and amount of sample (DPT) at deflagration in the improved time/ pressure test
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

(2) Method of Ignition

The method of ignition may affect deflagration. Table 3.23 shows comprehensively the comparison of the standard method (Nichrome wire heater method with an igniter of 1g(minium: 70wt.%, silicon: 30wt.%) with the other methods. Table 3.23 shows there is no noticeable difference between the standard method (ignition below the sample using a Nichrome wire heater), igniting from the top of the sample using the Nichrome wire heater, and igniting in the middle of the sample using a fusehead. There is also no noticeable difference among the varying compositions of minium/silicon igniters, such as minium/silicon ratio of 70/30, 50/50 and 90/10 wt.%. In the case of samples that are comparatively easy to ignite, like AIBN and DPT, the amount of igniter does not affect the curves describing the increase in pressure. In the case of the samples not so easily ignited, however, the method of ignition may affect the curves.

(3) Thickness of the rupture disk

Table 3.24 shows how the thickness of the brass rupture disks affects the deflagration of the samples. The table shows that the pressure on the rupture disk increases as the thickness of the disk increases, but it does not indicate much difference in the rate of pressure increase.

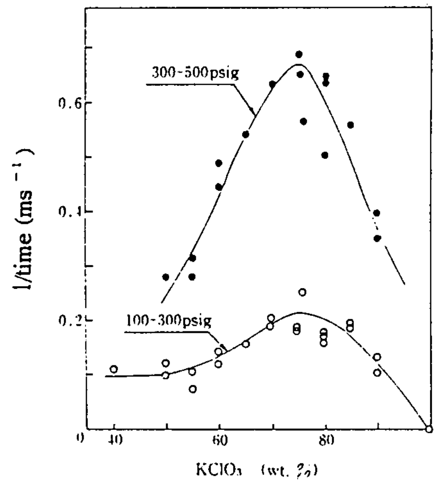


Fig. 3. 45 Effect of KClO $_3$ on deflagration rate of KClO $_3$ /cellulose A mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb $_3$ O $_4$ (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

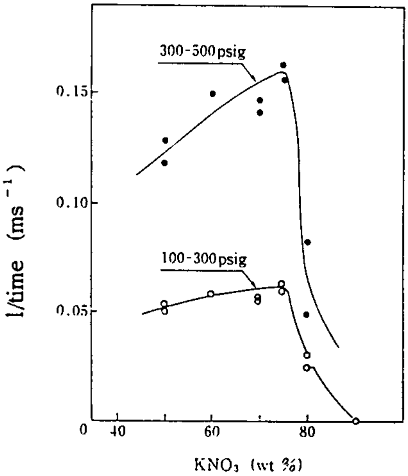


Fig. 3. 46 Effect of KNO $_3$ on deflagration rate of KNO $_3$ /cellulose A mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb $_3$ O $_4$ (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

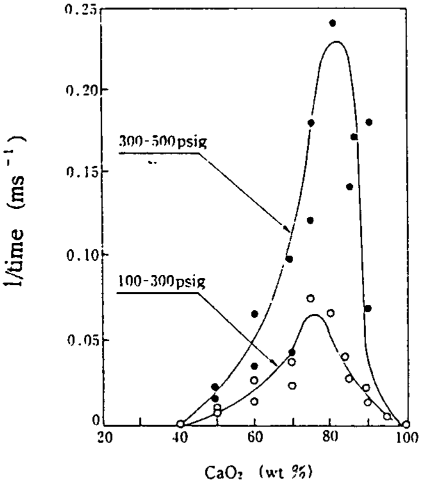


Fig. 3. 47 Effect of CaO $_2$ on deflagration rate of CaO $_2$ /cellulose A mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb $_3$ O $_4$ (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

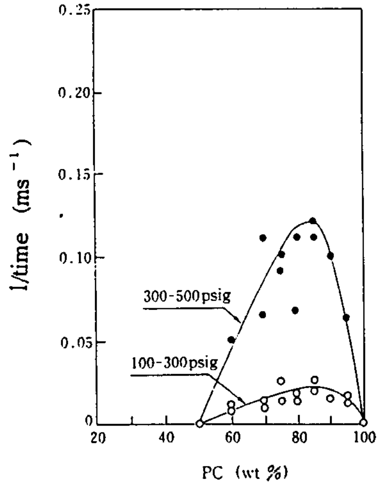


Fig. 3. 48 Effect of PC on deflagration rate of PC/cellulose A mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb $_3$ O $_4$ (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

Table 3.24 The effect of thickness of copper rupture disk on deflagration of black powder using modified time/pressure test

Thickness of rupture disk (mm)	Onset time of pressure (ms)		Rupturing pressure (psig)
	100-300psig	300-500psig	
0.10	0.86	0.31	866
	0.99	0.41	843
0.15	0.84	0.34	1424
	0.91	0.35	1353
0.20	0.97	-	-
	1.10	0.52	1960

(4) Amount of the sample

Fig.3.42 – 3.44 show how the amount of the sample affects deflagration. In all cases the rate of the increase in pressure rises with the size of the sample. The inverse values of the time interval for the pressure to rise from 690kPa (100psig) to 2,070 kPa (300psig) and from 2,070 kPa to 3,450 kPa (500psig) are proportional to the size of the sample tested. This indicates the possibility of assessing deflagration rate by using reduced quantities of sample.

Although the HSE [52, 84] method only uses the time interval associated with the rise in pressure from 690kPa(100psig) to 2,070kPa (300psig), in case of a slower rate of pressure increase, it is difficult to measure the time interval itself; the time interval for the pressure increase from 2,070kPa (300psig) to 3,450kPa (500psig) is also shown on the figures.

Summarizing all the above, the improved time/pressure testing method is advantageous for assessing the deflagration rate from the rate of pressure increase because reduced quantities of samples may be used. The standard test method established is to use 1 – 5g of igniter (minium : 70wt.%, silicon : 30wt.%) fired by a Nichrome wire heater that ignites a 5g sample laid on top of it and for which a 0.15mm thick brass rupture disk is used. It is recommended that the time intervals be measured as the pressure rises from 690kPa (100psig) to 2,070kPa (300psig) and from 2,070 kPa (300psig) to 3,450kPa (500psig).

K.7.2 Mixture of oxidizing agent and flammable material [82, 85-88]

(1) The ratio of a mixture to the deflagration rate

The deflagration rate of a mixture at the time of ignition may vary as the ratio of the composition of the mixture changes. Fig.3.45 – 3.48 show how the ratio of the composition of a mixture affects the deflagration rate in the case of a closed system containing a mixture composed of oxidizer/cellulose, in which cellulose A is selected as the flammable component, and either calcium peroxide and sodium carbonate − hydrogen peroxide or potassium chlorate, potassium nitrate and potassium dichromate are selected as typical inorganic oxidizers.

The degree of deflagration varies as a function of the type of oxidizer. Each mixture has its own deflagration rate and a specific composition which gives a maximum deflagration rate.

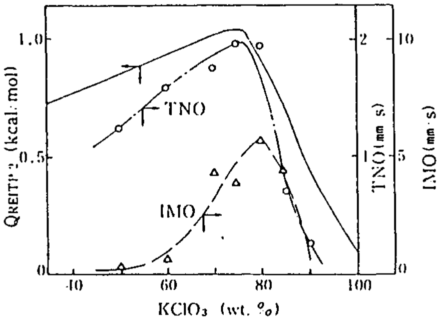


Fig. 3. 49 Effect of KClO$_3$ on the heat of reaction calculated by REITP−2 (QREITP−2), on the TNO detonation velocity, and on the IMO combustion rate of KClO$_3$/cellulose

In the case of a potassium di−chromate/cellulose mixture, there is no notable pressure increase under standard conditions.

To compare with this method, the heat of reaction calculated by REITP−2 [89], the combustion rate at the time of ignition under open conditions [93, 94] in the IMO combustion rate tests [90-92], and the combustion rate under conditions of partial enclosure [93, 94] in the TNO deflagration tests [95] are shown along with variations in the composition of the mixtures in Fig.3.49.

From these three sources of information the peak value of the rate of pressure increase due to deflagration of mixtures of oxidizers and flammable substances is given at the maximum heat of reaction, and a similarity is found between the open systems in the IMO combustion rate test and the partially enclosed systems in the TNO deflagration test.

It is therefore necessary to assess the deflagration rate associated with a composition that gives the maximum heat of reaction according to the REITP−2 calculation from the point of view of hazard assessment of the combination of the oxidizer with the flammable material.

(2) Type of oxidizer and deflagration rate

Cellulose A was selected as a typical flammable material, and the rate of pressure increase due to the deflagration of the flammable substance in combination with various oxidizers was tested. The results in comparison with the type of oxidizer are shown in Table 3.25. Effects of the oxidizers on the deflagration rate are evaluated as follows;

Table 3.25 The effect of oxidizers on deflagration of mixtures of oxidizer–combustible

Oxidizer	Content of oxidizer (wt.%)	Time(ms)	
		100-300psig	300-500psig
NH_4ClO_4	81	0.49	-
$NaClO_4$	70	4.6	1.4
$KClO_4$	70	4.7	2.1
$NaClO_3$	70	3.4	0.97
$KClO_3$	70	5.1	1.6
$KMnO_4$	85	38	26
$K_2Cr_2O_7$	85	No propagation	
NH_4NO_3	80	37	12
$LiNO_3$	60	105	43
$NaNO_3$	65	12	5.0
KNO_3	75	18	10
$CsNO_3$	70	25	13
$Mg(NO_3)_2$	65	No propagation	
$Ca(NO_3)_2$	65	No ignition	
$Sr(NO_3)_2$	70	186	82
$Ba(NO_3)_2$	80	No ignition	
$Cr(NO_3)_2$	70	No ignition	
$Co(NO_3)_2$	70	No propagation	
$Ni(NO_3)_2$	70	No propagation	
$CuNO_3$	65	No propagation	
$AgNO_3$	75	247	118
$Zn(NO_3)_2$	70	No ignition	
$Al(NO_3)_3$	70	No ignition	
$Pb(NO_3)_2$	75	No propagation	
$NaNO_2$	70	51	27
KNO_2	75	16	9
Na_2O_2	86	3.8	-
MgO_2	89	No ignition	
CaO_2	88	41	44
SrO_2	90	19	7.0
BaO_2	94	15	-
ZnO_2	93	14	12
PbO_2	90	No propagation	
$(NH_4)_2S_2O_8$	100	No prapagation	
$Na_2S_2O_8$	95	No propagation	
$K_2S_2O_8$	95	No propagation	
$2KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$	96	No ignition	
$2Na_2CO_3 \cdot 3H_2O_2$	90	120	35
$NaBO_2 \cdot H_2O_2$	89	No ignition	
$NaBO_2 \cdot H_2O_2 \cdot 3H_2O$	92	No ignition	
$4Na_2SO_4 \cdot NaCl \cdot 2H_2O_2$	96	No ignition	
$K_2SO_4 \cdot 2KHSO_4 \cdot H_2O_2$	97	No ignition	
$(NH_2)_2CO \cdot H_2O_2$	100	When sample was put in the vessel, it reacted and decomposed with ignitor	
$4(NH_2)_2CO \cdot CaSO_4 \cdot 4H_2O_2$	100	No ignition	
$C_3N_3(NH_2)_3 \cdot H_2O_2$	100	No ignition	

Sample: Mixtures of oxidizer–cellulose A, 5g
Ignitor: Pb_3O_4 (70wt.%)–Si(30wt.%), 1g
Igniting method: Nichrome wire heater, ignition from below.

1 : Oxohalogenic acid salt compounds show vigorous deflagration. Chlorate in comparison with perchlorate, and sodium salts in comparison with potassium salts, show stronger tendencies.

2 : For salts of nitric acid: while sodium salts, potassium salts,cesium salts, and ammonium salts show comparatively vigorous deflagration, lithium salts, strontium salts and silver salts show milder deflagration. Other metal salts of acids show almost no increase in pressure due to ignition.

3 : Potassium nitrite and potassium nitrate show approximately the same deflagration rate, but sodium nitrite shows comparatively lower deflagration rate than sodium nitrate.

4 : In the case of potassium permanganate, the deflagration rate is comparatively high; potassium di–chromate, however, does not show any increase in pressure but ignites.

5 : Metal peroxides show comparatively strong deflagration. This is especially the case for sodium peroxide. For peroxides of alkaline earth metals, the vigorousness of deflagration takes place with the following order of strength: barium peroxide > strontium peroxide > calcium peroxide > magnesium peroxide

6 : Peroxosulfuric acid salts show either no ignition or little increase in pressure after ignition.

7 : For hydrogen peroxide addition products, some deflagration was observed in the case of sodium carbonate–hydrogen peroxide addition products, but all others show either no ignition or little increase in pressure after ignition.

(3) Type of flammable material and deflagration rate

Potassium nitrate and sodium carbonate–hydrogen peroxide addition products are selected as typical oxidizers, and various flammable materials in combination with the oxidizers selected were tested for deflagration rate. The results in comparison with the oxidizers are shown in Table 3.26. Effects of the flammables on the deflagration for selected oxidizers are evaluated as follows;

1 : Red phosphorus as a flammable substance shows very strong deflagration, and aluminium powder is rated next.

2 : Cellulose A, selected as a flammable for comparison purposes in the deflagration ratings, was rated lower than red phosphorus, aluminium powder, hemp charcoal, dextrose, and sorbitol, was comparable to activated carbon and wood chips, and was stronger than granulated sugar, silicon, sulfur, titanium, and naphthalene.

(4) Materials in fireworks mixtures and deflagration rate

Various mixtures of materials in fireworks were tested for deflagration. The results are shown in Table 3.27. Changes in the rate of pressure increase vary with the amount of sample tested, so that those known to deflagrate strongly were evaluated with 1g samples.

Table 3.26 The effect of combustibles of deflagration of mixtures of oxidizer–combustible

Combustible	Content of oxidizer(wt.%)	Time(ms) 100-300psig	300-500psig
KNO_3-combustible mixtures			
red phosphorus	70	0.057	0.006
alumilium powder	65	1.1	0.5
charcoal	87	10	4.0
cellulose A	80	52	28
active carbon	80	64	22
wood powder	80	70	35
silicon	70	97	-
sulfur	79	97	-
titan(80 mesh)	62	No propagation	
naphthalene	80	No ignition	
PC-combustible mixtures			
dextrose	89	37	15
sorbitol	88	70	20
cellulose A	90	120	31
granulated suger	85	160	130
charcoal	95	93	20
citric acid	84	No propagation	
sodium dodecylbenzenesulfonate	94	No propagation	
polyethylene glycolmonostearate	93	No propagation	

Sample: KNO_3 –combustible mixtures or PC–combustible mixtures, 5g
Ignitor: Pb_3O_4 (70wt.%)–Si(30wt.%), 1g
Igniting method: Nichrome wire heater, ignition from below.

Table 3.27 shows the effects of various oxidizers on the deflagration rate of hemp charcoal. Similarly to the case where cellulose A was used as a flammable material for the tests, hemp charcoal shows very strong deflagration with oxohalogenates; especially noteworthy is the case with ammonium perchlorate. It is also noticeable that the deflagration of the samples is all strong because of the hemp charcoal, which is known to be more powerful in deflagration than cellulose A. For example, the time interval for the pressure increase from 690kPa (100psig) to 2,070kPa (300psig) in the case of $Sr(NO_3)_2$/cellulose was about 190ms, while $Sr(NO_3)_2$/hemp charcoal was considerably shorter at only 14ms. The $KClO_4$ / Al/Ti series of firework materials exhibited very powerful deflagration, even if only 1g of the sample was used for the test.

It is quite important to assess how strong the deflagration rate is at the time of ignition for high energy materials like explosives, but a simple, suitable way to assess this quantitatively is not known. For this purpose the improved time/pressure test method can be applied. This test method, however, has been developed to determine the

Table 3.27 Deflagration properties of pyrotechnic raw compositions using modified time/pressure test

Sample mass (g)		1		5		5	
Ignitor (g)		1		1		2	
Pressure range (psig)		100-300	300-500	100-300	300-500	100-300	300-500
Oxidizer (wt.%)	Combustible (wt.%)	Time (ms)					
NH_4ClO_4 (90)	charcoal (10)	1.3	0.4				
$KClO_4$ (85)	charcoal (15)	3.2	1.0				
$KClO_3$ (87)	charcoal (13)	4.6	1.9	0.6	0.3		
KNO_3 (87)	charcoal (13)	5.0	3.1	10.0	4.0		
$Sr(NO_3)_2$ (88)	charcoal (12)	No prop.		13.6	5.9		
$Ba(NO_3)_2$ (91)	charcoal (9)	No ign.		35.0	10.0	41.0	15.8
Pb_3O_4 (96)	charcoal (4)			No ign.			
KNO_3 (65)	Al powder (35)	4.5	5.0	1.1	0.5		
		6.8	8.7				
KNO_3 (62)	Ti_a (38)			No prop.		52.0	-
$KClO_4$ (72)	Al(14)+Ti_a(14)	0.6	0.1				
$KClO_4$ (72)	Al(14)+Ti_b(14)	0.7	0.2				
$KClO_4$ (67)	Al(20)+S (13)	0.6	0.03				

Sample: Oxidizer–combustible mixtures, 1g or 5g

Ignitor: Pb_3O_4 (70wt.%)–Si(30wt.%), 1g or 2g

Igniting method: Nichrome wire heater, ignition from below.

K.7.3 Explosives 88, 96)

deflagration rating of reactive chemicals 52, 81, 82, 84) . An application of the method to substances that can detonate like explosives may present safety problems.

Considerations should be made to reduce the deflagration rate of such high energy materials like explosives by adding some inactive filler to the test samples. The tests could then be run under milder conditions so that the sample would not detonate while the tests were being conducted. To make the tests possible, first the dilution effect of the fillers was evaluated by using the improved time/pressure test rig. Second, the intended tests for the filler mixed with explosives were carried out, and an assessment was made from the rates of pressure increase for the explosives evaluated.

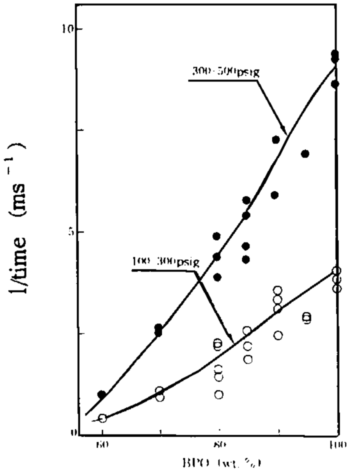


Fig. 3. 50 Effect of CaCO 3 on deflagration rate of CaCO 3 /BPO mixtures in the improved time/ pressure test
Sample quantity : 5g
Igniter : Pb 3 O 4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

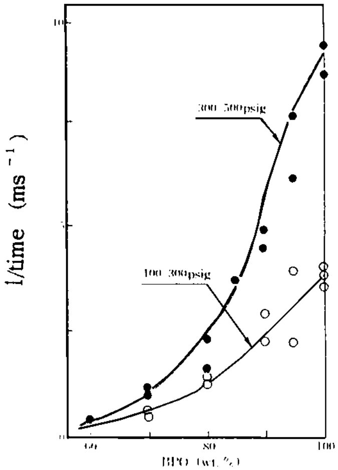


Fig. 3. 51 Effect of Talc on deflagration rate of Talc/BPO mixtures in the improved time/ pressure test
Sample quantity : 5g
Igniter : Pb 3 O 4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

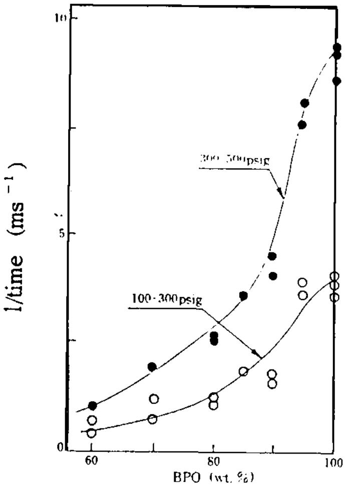


Fig. 3. 52 Effect of Al 2 O 3 on deflagration rate of Al 2 O 3 /BPO mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb 3 O 4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

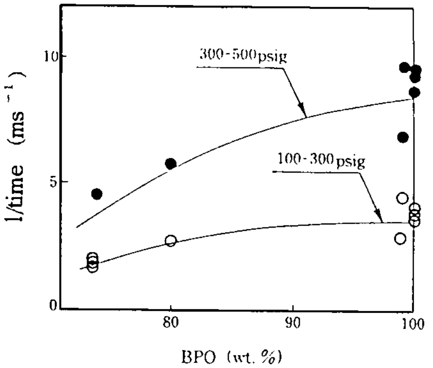


Fig. 3. 53 Effect of water on deflagration rate of water/BPO mixtures by improved time/pressure test
Sample quantity : 5g
Igniter : Pb 3 O 4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

(1) The dilution effect of fillers on the deflagration of explosives

To evaluate the difference in dilution effects among various inactive fillers, benzoyl peroxide (BPO) was selected for the test of deflagration rates of the BPO−filler series.

Various combinations of the BPO−$CaCO_3$ series, the BPO−talcum powder series, the BPO−Al_2O_3 series and the BPO−water series were tested to measure the time of pressure increase from 690kPa (100psig) to 2,070kPa (300psig). The results of the comparison of various filler rates are shown in Fig.3.50 − 3.53.

The figures show that the rate of pressure increase due to the deflagration rate was retarded in all cases by adding fillers to BPO, with some variation depending on the kind of fillers used. For a particular filler used in any of the filler mixed compositions, no abnormal deflagration was observed. Therefore, the fillers tested may be used as inert fillers.

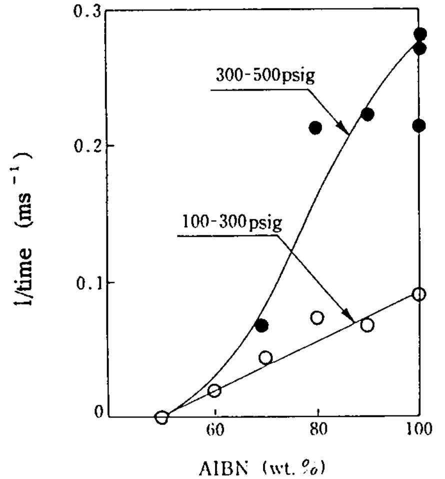


Fig. 3. 54 Effect of $CaCO_3$ on deflagration rate of $CaCO_3$/AIBN mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt.%) / Si (30wt.%), 1g
Method of ignition : Nichrome wire at bottom

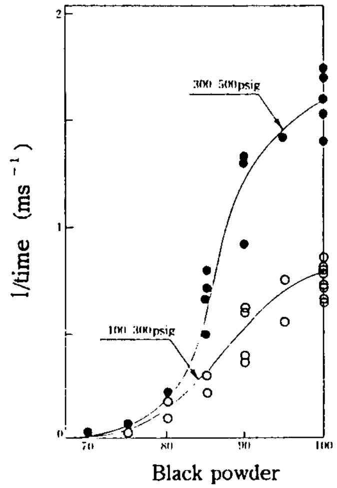


Fig. 3. 55 Effect of $CaCO_3$ on deflagration rate of $CaCO_3$/gunpowder mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt.%) / Si (30wt.%), 1g
Method of ignition : Nichrome wire at bottom

To present the effects of various high energy substances along with the filler dilution effects, $CaCO_3$ was selected as the filler and azobisisobutyrlnitrile (AIBN), gunpowder, and trinitrotoluene (TNT) were selected for the high energy substances for tests. The deflagration rates are shown in comparison with BPO in Fig.3.54− 3.56. The figures show that for the mixtures with $CaCO_3$ filler, the rate of pressure increase due to deflagration tends to be retarded. There are no noticable differences between the high energy substances tested except for TNT, which showed a milder deflagration. In other words, the $CaCO_3$ filler can be effectively used as an inert filler regardless of the kind of high energy substances tested.

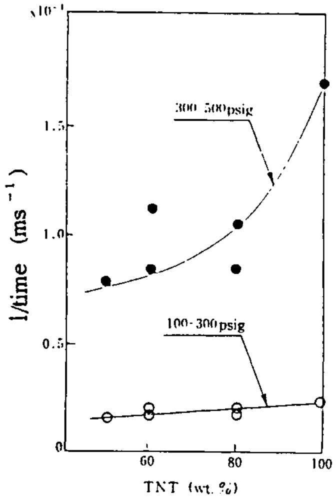


Fig. 3.56 Effect of $CaCO_3$ on deflagration rate of $CaCO_3$/TNT mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt.%) / Si (30wt.%), 1g
Method of ignition : Nichrome wire at bottom

In summary, if an inert filler is added to the high energy substances to be tested, an abnormal deflagration can be eliminated by the retarding effect of the filler. Therefore, the filler diluting method may be used as a way of assessing the relative hazards of high energy substances.

(2) Explosives-$CaCO_3$ series of compositions and deflagration rate

The deflagation rates of explosives under consideration after the addition of 30 wt.% $CaCO_3$ as an inert filler are shown in Table 3.28. Among these substances cyclotrimethylenetrinitramine (RDX), pentaerithrytoltetranitrate (PETN), and black carlit show the most vigorous deflagration; the next are gunpowder, 2,4,6-tetranitro-N-methylaniline (Tetryl) and pentlite; picric acid and TNT are considerably milder in deflagration under the testing conditions.

Table 3.28 Deflagration properties of mixtures of high energetic materials with filler using modified time/pressure test

High energetic materials	Filler	Onset time of pressure(ms)	
		100-300psig	300-500psig
BPO	$CaCO_3$	2.1	0.8
	talc	1.9	1.0
	Al_2O_3	0.7	0.4
	H_2O	1.0	0.4
AIBN	$CaCO_3$	21.6	15.5
Black powder	$CaCO_3$	4.2	3.3
TNT	$CaCO_3$	55.6	11.0
PETN	$CaCO_3$	4.8	1.1
		9.0	2.7
RDX	$CaCO_3$	1.7	0.5
Tetryl	$CaCO_3$	7.5	2.4
		13.7	3.4
Pentolite(50/50)	$CaCO_3$	9.9	2.9
		10.9	2.6
No.5 black carlit	$CaCO_3$	4.8	1.3

Sample: Mixtures of high energetic materials with filler, 1g or 5g
Ignitor: Pb_3O_4 (70wt.%)-Si(30wt.%), 1g
Igniting method: Nichrome wire heater, ignition from below.

K.7.4 Organic peroxides [83, 88]

(1) Comparison of solid and liquid samples in testing

Organic peroxides are commonly liquids. Testing liquid samples is conducted with a rig especially made for handling liquids. A fusehead is used for liquids in place of the Nichrome wire heater for solid samples.

The differences noted in deflagration hazards as a function of the methods of ignition (either by a fuse head or by a Nichrome wire heater) have been examined and are shown in Table 3.29. No noticable difference in the rate of pressure increase due to deflagration was obserbed for either of the methods of ignition. No effect in the assessment of deflagration hazard was observed when polyvinylidene films were used for wrapping the igniters and the samples.

Table 3.29 The effect of ignition methods on deflagration of organic peroxides using modified time/pressure test

Ignitor (g)		1		3	
Pressure range (psig)		100-300	300-500	100-300	300-500
Organic peroxides (active oxygen(wt.%))	Ignition method	Onset time of pressure (ms)			
Benzoyl peroxide (6.61)	NC,B	0.33	0.15	0.42	0.14
	FH,C	0.40	0.19	0.36	0.14
2,5-Dimethyl-2,5-di (benzoyl peroxy) hexane(8.03)	NC,B	13	5.6	12	4.8
	FH,C	14	4.4	13	4.7
2,5-Dimethylhexane-2,5-dihydroperoxide(14.29)	NC,B	58	31	67	32
	FH,C	100	21	120	31

Sample: 5g, Ignitor: Pb_3O_4 (70wt.%)–Si(30wt.%), 1g or 3g
NC,B: Nichrome wire heater, ignition from below,
FH,C: Fusehead, ignition in center.

(2) Sensitivity of ignition and rate of pressure increase due to deflagration

Some organic peroxides have lower sensitivity to ignition than others. To assess the deflagration hazard of such materials, the amount of igniter used must be adjusted to find a vigorous deflagration that yields a peak value for the rate of pressure increase. The sensitivity of ignition is determined from the amount of igniter which gives this peak value.

Fig.3.57 shows the relationship between the amount of igniter and the rates of pressure increase for some typical organic peroxides having different levels of hazards associated with their deflagration. As shown in the figure, benzoylperoxide and a,a'–bis (t–butylperoxy–p–isopropyl) benzene are considered to possess a high ignition sensitivity because they give the maximum rate with only 1g of igniter. On the other hand, t–butylisopropylcarbonate is considered comparatively lower in sensitivity, because it needs as much as 4g of igniter to reach the maximum rate of pressure increase. In the case of benzoylperoxide, the peak value of the rate of pressure increase is high, while t−butyl peroxyisopropyl carbonate has a lower peak value, indicating less vigorous deflagration.

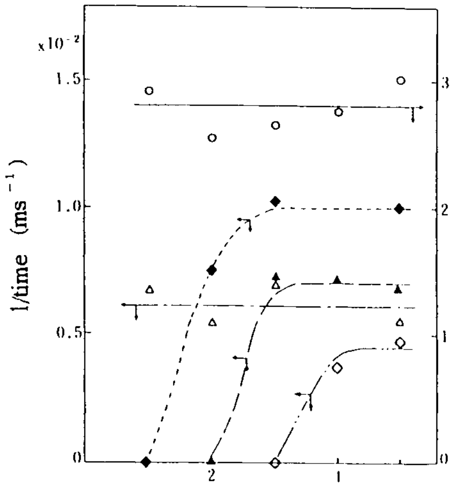


Fig. 3. 57 Effect of igniter on deflagration rate of organic peroxides in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition: Nichrome wire at bottom
or fusehead at center
○ : Benzoylperoxide
△ : a, a'−bis(t−butylperoxy−p−isopropyl)benzene
▲ : Di−t−butylperoxyisopropylcarbonate
◆ : n−butyl−4, 4'−bis(t−butylperoxy)valerate

(3) The ignition sensitivity of organic peroxides and the vigorousness of deflagration

The value for the hazard of deflagration of an organic peroxide is assessed in terms of deflagrability (sensitivity) and deflagration rate (vigorousness) shown in Table 3.30. The amount of igniter shown in Table 3.30 is that which causes the peak value in the rate of pressure increase. The smaller the amount of igniter, the higher the sensitivity of the compound. The time intervals shown correspond to that amount of igniter. The less time required, the more vigorous the deflagration.

From the results shown in Table 3.30, benzoylperoxide, di−t−butylperoxyisophthalate, 2,5−dimethyl−2,5−di(benzoylperoxy)hexane and t−butylperoxymaleic acid have a time interval over which the pressure rises from 690kPa (400psig) to 2,070kPa (300psig) that is less than 30ms. They are considered very vigorous in deflagration, and their sensitivity is also high.

The ignition sensitivity (measured by the amount of igniter that yields the peak value for the rate of pressure increase) and the rate of preasure increase due to the deflagration (taken as the logarithmic value of the inverse of the time interval over which the pressure rises from 690kPa (100psig) to 2,070kPa (300psig)) along with the amount of active oxygen for each type of organic peroxide are shown in Fig.3.58 and Fig.3.59.

From the figures, the sensitivity of each type of organic peroxide increases as the amount of active oxygen in the substance increases, and the rate of pressure increase due to deflagration also increases. Also for each type of organic peroxide, for a given amount of active oxygen in a given substance, the ignition sensitivity is high and rate of

Table 3.30 Results of organic peroxides using modified time/pressure test

Organic peroxides	Purity (wt.%)	Active oxygen[a] (wt.%)	State	Ignitor mass[b] (g)	Deflag. property Onset time (ms) 100-300	300-500ps
1.Dialkyl peroxides						
Di-t-butylperoxide	99.0	10.83	liquid	3	140	32
t-Butylcumylperoxide	90.1	6.92	liquid	5	No deflagration	
Dicumylperoxide	98.0	5.80	flake	5	No deflagration	
α,α'-Bis(t-butyl-peroxy)-diisopropyl benzene	99.0	9.38	flake	1	160	70
2,5-dimethyl-2,5-di-(t-butylperoxy)hexane	90.1	9.93	liquid	5	No deflagration	
2,5-dimethyl-2,5-di-(t-butylperoxy)hexyne-3	93.8	10.48	liquid	1	56	13
2.Diacylperoxides						
Decanoylperxide	98.0	4.58	powder	5	No deflagration	
Lauroylperoxide	99.3	3.98	flake	5	No deflagration	
Benzoylperoxide	99.9	6.61	powder	1	0.33	0.15
3,5,5-trimethyl-hexanoylperoxide	75.0	3.82	liquid	5	No deflagration	
3.Hydroperoxides						
t-Butylhydroperoxide	80.6	14.31	liquid	1	160	54
Cumenehydroperoxide	82.0	8.62	liquid (hydrocarbon solution)	5	No deflagration	
Diisopropylbenzene hydroperoxide	54.0	4.45	liquid (hydrocarbon solution)	5	No deflagration	
P-menthanehydro-peroxide	52.7	4.90	liquid (hydrocarbon solution)	5	No deflagration	
2,5-Dimethylhexane-2,5-dihydroperoxide	79.6	14.29	powder (20wt.%:H_2O)	1	82	30
4.Peroxyesters						
t-Butylperoxybenzoate	99.0	8.16	liquid	1	120	13
Di-t-Butyldiperoxy isophtalate	82.0	8.45	powder (20wt.%:H_2O)	1	4.4	1.3
2,5-Dimethyl-2,5-di(benzoylperoxy)hexane	97.0	8.03	powder	1	13	4.9
t-Butylperoxy maleic acid	98.8	8.40	powder	1	5.9	1.9
t-Butylperoxy isopropylcarbonate	98.0	8.90	liquid	4	230	37
t-Butylperoxylaurate	99.1	5.28	liquid	5	No deflagration	
t-Butylperoxypivalate	70.0	6.43	liquid	5	No deflagration	
5.Others						
1,1-Bis(t-butylper-3,3,5-trimethylcyclohexane	90.1	9.54	liquid	1	50	21
n-Butyl 4,4-bis-(t-Butylperoxy)valerate	88.2	8.44	liquid	2	120	36
Methylethylketone peroxide	56.6	10.30	liquid	1	97	42

a: Active oxygen(wt.%)=(atom mass of oxygen × number of −O−O−) × purity / molecular weight

b: Ignitor mass at maximum rising rate of pressure

Sample mass: 5g, ignitor: Pb_3O_4 (70wt.%)−Si(30wt.%),
Igniting method: Nichrome wire heater, ignition from below or fusehead, ignition from center.

pressure increase is large.

From this observation the relative hazards of deflagration for these substances is given in the following order: diacylperoxide> peroxyester > dialkylperoxide > hydroperoxide

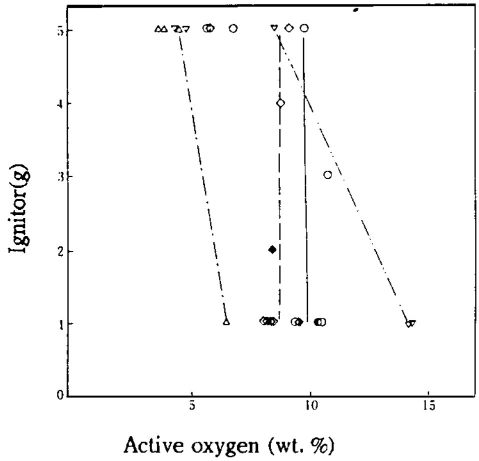


Fig. 3. 58 Effect of amount of active oxygen vs. amount of igniter that results in the maximum rate of pressure increase at deflagration of organic peroxides in the improved time/pressure test

Sample quantity : 5g

Igniter : Pb3O4 (70wt. %) / Si (30wt. %), 1g

Method of ignition: Nichrome wire at bottom or fusehead at center

○ : Dialkylperoxide
△ : Diacylperoxide
◇ : Peroxyester
◆ : Peroxyketal
▽ : Hydroperoxide
● : Ketoperoxide

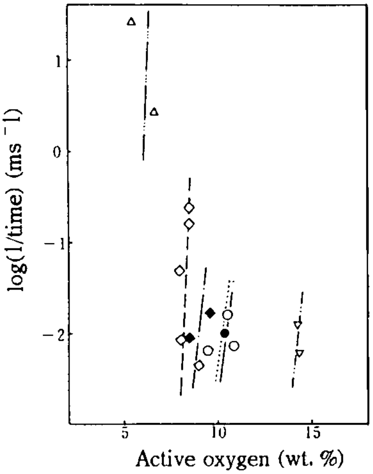


Fig. 3. 59 Effect of amount of active oxygen that results in the maximum rate of pressure increase at deflagration of organic peroxides in the improved time/pressure test

Sample quantity : 5g

Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g

Method of ignition: Nichrome wire at bottom or fusehead at center

○ : Dialkylperoxide
△ : Diacylperoxide
◇ : Peroxyester
◆ : Peroxyketal
▽ : Hydroperoxide
● : Ketoperoxide

K.7.5 Effects of granular size 97)

By the use of the improved time/pressure testing rig, an assessment of the hazard of deflagration has been made for a series of chemicals as mixtures of oxidizers and flammable substances, 82, 85-88), explosives 88, 96) and organic peroxides 83, 88). Many of the compounds evaluated in these tests are solids, and it is thought that the hazard associated with deflagration may be affected by the granular size of the samples tested. It is, therefore, important to determine if the size of the grains affects the test results.

(1) Granular size effects on the deflagration rate of single compounds

BPO and AIBN were selected as the compounds for this study; they have different rates of deflagration, and they have been evaluated to determine the effects of the granular size on the deflagration rate. The results of these tests are shown in Fig. 3.60. The data in the figure indicates that, as far as the compounds BPO and AIBN are concerned, the average rate of pressure increase rises as the granular size becomes larger. Therefore, the deflagration hazard increases as grain size increases.

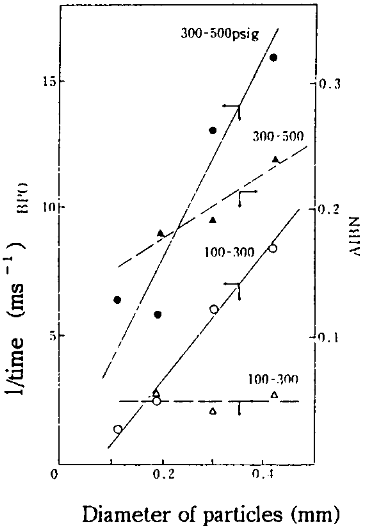


Fig. 3. 60 Effect of granule size on deflagration of BPO and AIBN in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

(2) Granular size effects on deflagration rates of mixtures of oxidizers with flammable materials

To find the effects of granular size on the deflagration rate of mixtures of oxidizers and flammable materials, mixtures of substances having a range of granular sizes are tested, and rates of pressure increase due to the deflagration are examined.

Cellulose (geometric average granular diameter (GAGD) 0.11mm) as the flammable component and $KClO_3$, KNO_3 and PC in various sizes of granules as the oxidizer are selected, and the results are shown in Fig.3.61. Another series of the tests are carried out using sorbitol (GAGD 0.11mm) as the flammable component with the same oxidizers used in the previous tests. The results are shown in Fig. 3.62. The figure indicates that, contrary to previous tests using the single compounds, for mixtures of oxidixers and flammables as test samples, the rate of pressure increase goes up as the granular size becomes smaller. Fig. 3.61 and Fig. 3.62 also show that compositions having higher rates of pressure increase upon deflagration, like those in which $KClO_3$ and KNO_3 are oxidizers, present a stronger tendency toward increasing rates than mixtures of PC, which has a lower rate of pressure increase in deflagration.

Another series of tests has been conducted with particles of a fixed GAGD of 0.11mm for the oxidizers used and a changing granular size of the particles of flammables, sorbitol and cellulose. The results are shown in Fig. 3.63. In this case, the closer the granular size of flammables to that of the oxidizers, the larger the rate of pressure increase due to the deflagration. Here again the trend in the effects is larger with the oxidizer KNO_3 and smaller with PC.

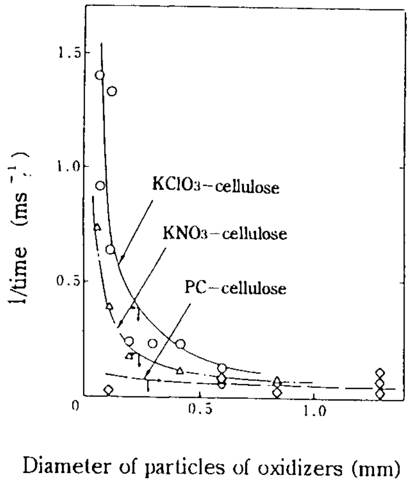


Fig. 3. 61 Effect of granule size of oxidizer on deflagration of oxidizer/cellulose mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb $_3$O$_4$ (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

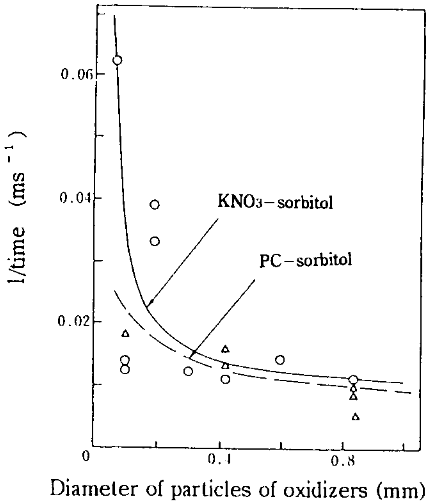


Fig. 3. 62 Effect of granule size of oxidizer on deflagration of oxidizer/sorbitol mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb $_3$O$_4$ (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

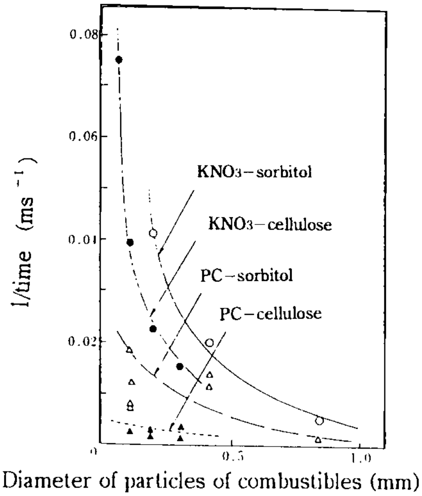


Fig. 3. 63 Effect of granule size of flammable materials on deflagration of oxidizer/flammable mixtures in the improved time/ pressure test
Sample quantity : 5g
Igniter : Pb $_3$O$_4$ (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

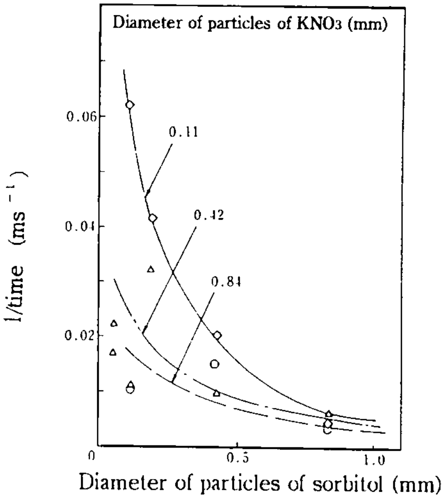


Fig. 3. 64 Effect of granule size of sorbitol on deflagration of KNO $_3$ /sorbitol mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb $_3$O$_4$ (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

In the next series of the tests, the GAGD of both KNO_3 and sorbitol are selected at 0.11mm, 0.42mm and 0.84mm. The results from the improved time/pressure test are shown in Fig.3.64, Fig.3.65 and Fig.3.66. These figures demonstrate that the smaller the granular size of the samples, the larger the rate of pressure increase due to the deflagration. The trend in effects is larger for the smaller granular sizes of both KNO_3 and sorbitol.

(3) A study of the effects of granular size on the deflagration rate of mixtures and single compounds

The rate of pressure increase due to deflagration increases as the granular size becomes larger in the case of single compounds, while the trend is reversed in the case of mixtures of oxidizers and flammable materials. Under closed conditions as in the improved time/pressure test device, the factors considered in the granular size effect on the deflagration rate for the single compounds are the sizes of granules, the surface area of the granules, and the volume ratio of the compounds. In the case of the single compounds, the larger the granule size, the larger the influence on the propagation of deflagration. As the surface area becomes smaller and the void volume larger, the inter-granular propagating speed of deflagration is retarded. The small volume of air in the closed system should not increase the deflagration rate, so the increase in deflagration rate for a single compound with increasing in size of granules should be controlled by the inter-granule deflagration rate.

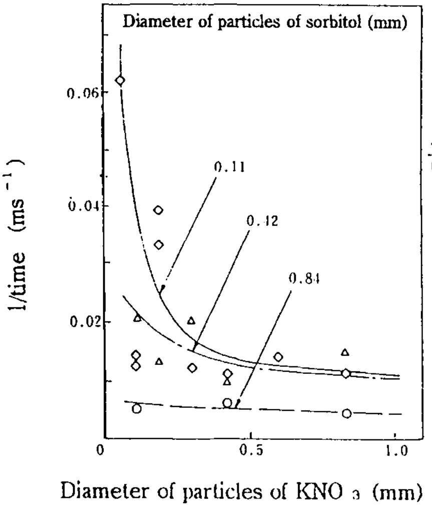


Fig. 3. 65 Effect of granule size of KNO_3 on deflagration of KNO_3 / sorbitol mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

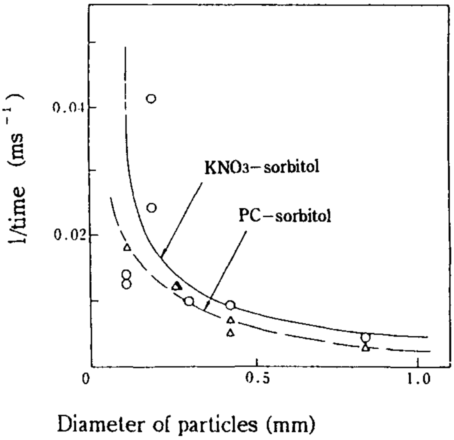


Fig. 3. 66 Effect of granule size on deflagration of oxidizer/sorbitol mixtures in the improved time/pressure test
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition : Nichrome wire at bottom

In case of mixtures of oxidizers and flammable materials, on the other hand, the effect of granular size upon the deflagration rate is more complex.

Everything cannot be explained with the given data regarding the effect of granule size upon the deflagration rate, but a deduction may be made about the reason for a noticable increase in the rate of pressure increase due to deflagration. Because the oxidizers and flammable solids have a larger surface area, the possibility exists that more oxygen, perhaps from pyrolytic decomposition of the oxidizer, may be supplied to the flammable material. Perhaps the oxidizer itself decomposes because of the initial heat of combustion generated by the flammable solid in the system.

Decrease in void volume due to the smaller granular size also may contribute to heat transfer in the pyrolitic decomposition process or to the supply of oxygen to the flammable maferial.

In any event, the mechanisms behind the effect of granular size upon the rate of pressure increase due to deflagration of both single compounds and mixtures of oxidizers and flammable materials are problems to be solved in the future.

K.7.6 Comparison with UN time/pressure test [98]

There are some variations in the improved time/pressure test in comparison to the UN test [52, 84]. How those variations affect the results generated by the UN test needs to be established. The following three methods are compared as shown in Table 3.31.

Fig.3.67 and Fig.3.68 show the results of the comparison of the improved time/pressure test [81, 82] with the improved time/pressure test in the Japan Carlit Method [98] and with the UN test [52, 84] respectively.

Table 3.31 Equipment of Time/Pressure Test (TPT) and ignition method

Test methods	Test equipment	Ignition methods
1.Modified TPT[81, 82]	Modified equipment	Pb_3O_4-Si ignitor
2.Modified TPT[98] (Nippon Carlit Co.)	UN equipment	Pb_3O_4-Si ignitor
3.UN TPT[52, 84]	UN equipment	KNO_3-Si ignitor (containing flax)

Due to the limited amount of data from the two improved time/pressure tests, not much detailed discussion can be offered. In the comparison with the Japan Carlit Method, there are some discrepancies in the region of the longer time intervals during the rate of pressure increase due to deflagration; i.e., the rate of pressure rise is somewhat smaller than observed in the other test. Overall, however, there is a fairly good agreement among the results for chemical compounds examined.

In comparison to the results of the UN test, the given data are limited only to the organic peroxides. A similar descrepancy shows up in the regions where the rate of pressure increase is lower, but the overall trends agree quite well. Especially in the region of possible explosion hazards due to deflagration as defined in the criteria given by the UN method (30ms or less for the pressure to rise from 690kPa (100psig) to 2,070kPa (300psig)),the agreement between the tests is so good that, as far as the intended purpose of hazard assessment is concerned, there exists no specific problem with any of the tests.

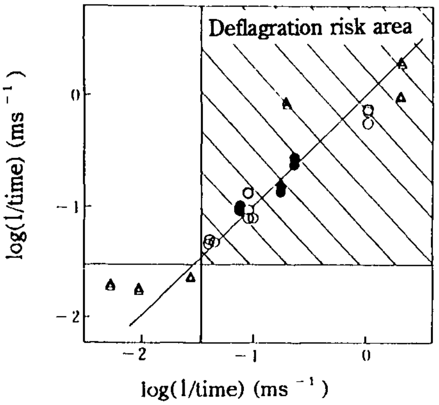


Fig. 3. 67 Comparison of data from The Japan Carlit test method and the improved time/pressure test
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition: Nichrome wire at bottom or fusehead at center
Time required T : 100−300psig in the improved time/pressure test
Time required T': 100−300psig in the The Japan Carlit test method

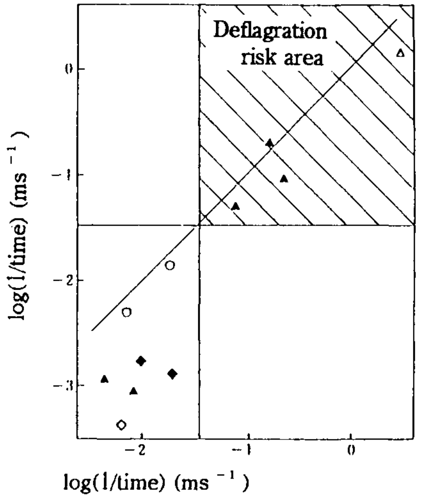


Fig. 3. 68 Comparison of deflagration data from the UN test method and the improved time/pressure test on organic peroxides
Sample quantity : 5g
Igniter : Pb_3O_4 (70wt. %) / Si (30wt. %), 1g
Method of ignition: Nichrome wire at bottom or fusehead at center
Time required T : 100−300psig in the improved time/pressure test
Time required T': 100−300psig in the the UN test method
○ : Dialkylperoxide
△ : Diacylperoxide
▲ : Peroxyester
◆ : Others

K.7.7 Some comparisons with other related test methods

The proposed improved time/pressure test is conducted under closed conditions and assesses the deflagration hazard from the rate of pressure increase observed [81-83]. It is, however, important to know in advance the differences between that and other

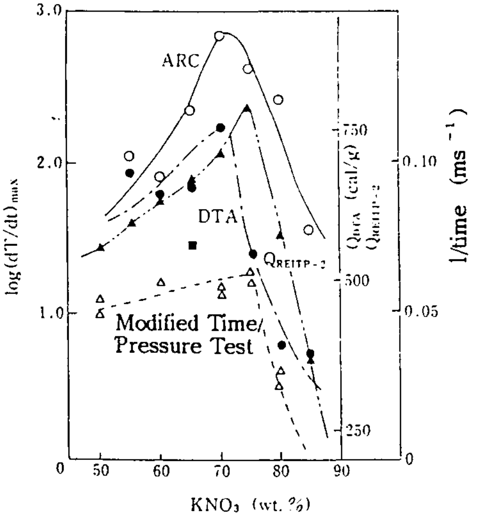


Fig. 3. 69 Effect of KNO 3 content on QDTA, on the maximum exothermal rate, on the rate of pressure increase (in improved time/pressure test), and QREITP−2 calculations.

tests, such as the methods of assessment of hazard from burning, of heat generating rate in a heated sample, and of the assessment of hazard during pyrolitic decomposition [99] by caloric values and rate of pressure increase.

(1) A comparison with other methods of hazard assessment by burning

As was discussed earier and shown in Fig.4.69, all three methods — the IMO burning rate test [93, 94], which evaluates hazards under atmospheric conditions, the TNO deflagration test [95], which is conducted under semi−closed conditions, and the improved time/pressure test, which is carried out under completely closed conditions — result in similar combustion hazard trends for samples [82, 85] with peak values existing near the zero point in terms of oxygen balance. This also agrees well with similar evaluations done by the calculations of heat of reaction using the REITP−2 program. The improved time/pressure test, in comparison with two other combustion hazard assessment methods, is applicapable to a hazard assessment of self−reactive substances that may pose combustion hazards over wide ranges of conditions with small quantities of materials.

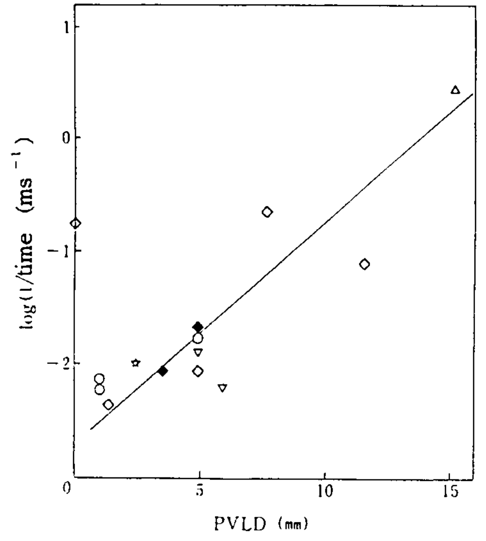


Fig. 3. 70 Relationship between PVLD in the pressure vessel test and deflagration rate in the improved time/pressure test on organic peroxides

○ : Dialkylperoxide
△ : Diacylperoxide
◇ : Peroxyester
◆ : Peroxyketal
▽ : Hydroperoxide
☆ : Ketoperoxide

(2) A comparison with the pyrolitic method of assessing hazard [99]

Results obtained from the DSC test (that evaluates the pyrolitic hazard during the heat generating period based on calculations from caloric values), from the ARC test (that evaluates hazards based upon heat generating rates or rates of pressure increase), and the improved time/pressure test (that assesses the deflagration hazard from the rate of pressure increase at the time of ignition), are shown in Fig. 3.69 together with the values of heats of reaction calculated by REITP−2. Also show is the similarity of results for trends of combustion hazards showing a maximum hazard near the zero point in oxygen balance.

Further, a relationship between the pressure vessel test (that assesses the pyrolitic hazard using the limited diameter (PVLD) that is considered to correspond to a rate of pressure increase during the heating process) and the improved time/pressure test applied to organic peroxides is shown in Fig.3.70. This suggests [83] a correlation between the results of the tests.

From the above discussions, notwithstanding the difference in the type of energy assessed by testing methods, for many reactive chemical substances the results of the evaluations show similar trends.

K.7.8 Analysis of deflagration by a visible time/pressure test [100]

To investigate further the validity of the improved time/pressure test method, a new device was introduced to make the inside of the chamber visible to enable direct observation of the tests. Deflagration phenomenon have been analyzed by the determination of deflagration rates as well as by the results of visible observation.

(1) The visible time/pressure rig

A quartz chamber that enables the observation of a deflagration test is used in the visible time/pressure test rig. A schematic is given in Fig. 3.71. The location of the ignition system, a Nichrome wire heater or a fusehead, is not the same as that in the improved time/pressure test rig. The other elements of the rig, such as the inner diameter of the chamber and the volume inside the chamber, are maintained.

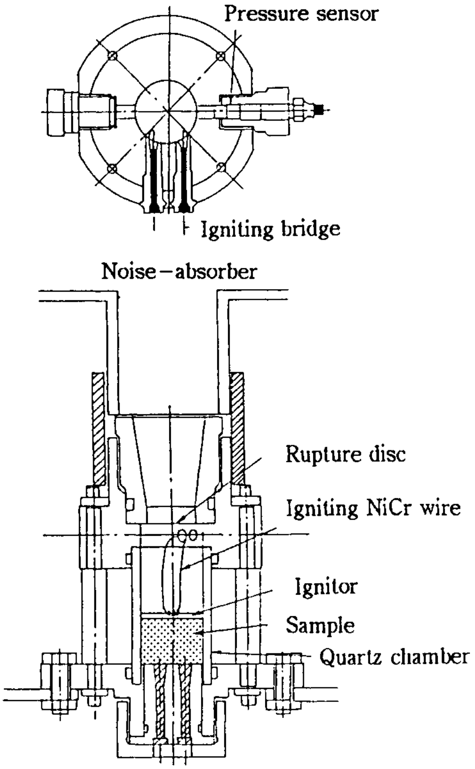


Fig. 3. 71 Visible time/pressure test rig

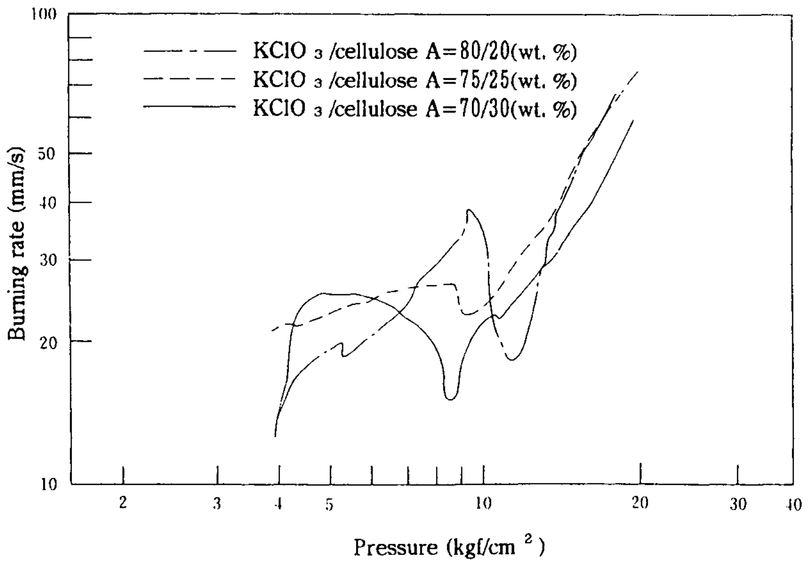


Fig. 3.72 Burning rate of $KClO_3$/cellulose mixtures

(2) Measuring system

Testing is conducted in a similar manner as with the improved time/pressure rig. The samples are ignited to cause deflagration, and the time intervals of pressure changes are measured. Observation by a high speed video is also carried out simulataneously during the tests.

A type 601A piezio sensor made by Kisler is used as a pressure probe, which leads to a type 5007 change amplifier, and the data are acquired by an R−510 data recorder made by TEAC. A HSV200 high speed video camera (200 frames per second) made by NAC completes the unit.

Some tests were conducted to find a linear deflagration rate by using 0.5 g samples of a $KClO_3$ /cellulose mixture packed in a slim quartz tube 6.65 mm i.d. installed in the visible test rig. The igniter (50 mg) was charged over the tube, and deflagration was initiated by ignition from above.

(3) Deflagration phenomena

In the visible time/pressure tests for the substances that have comparatively slow deflagration rates, such as AIBN and DPT, the deflagration progresses in the following manner: approximately 0.2 seconds after the start of deflagration, the deflagration spreads completely over the entire ignited material. The sample itself starts to melt at the surface and to release gases by burning near the igniter. An indigenous colored region (a homogeneous gray for AIBN, a black arborescent for DPT) develops. Due to the gases evolved from the sample, the combustion residue from the ignited material over the sample starts to erupt into the space above the igniter. The increase in pressure is noticeable during this period. Disruption of the sample follows with an accelerated increase in pressure, and finally the rupture disk bursts. The still−burning sample material erupts out through the plug where the rupture disk was loaded.

The substances that have larger deflagrating rates, on the other hand, like the mixtures of $KClO_3$ /cellulose, show the following progression: A glaring flame forms during the reaction of the flammable gases generated by the decomposition of cellulose and of the oxidizer, $KClO_3$, almost at the time of ignition. The flame front moves downward with elapsed time. Pressure rises as the flame front progresses. The relationship between the rate of pressure increase and the speed of propogation of the flame front expressed as logarithms are given in Fig. 3.72. Up to a pressure level of about 1,000kPa, the process involves the burning of igniter and may not represent the true deflagration. At pressures beyond this level, the deflagration develops vigorously with increasing pressure. The deflagration rate in this region is approximately proportional to the square of the rate of pressure increase.

(4) Analysis of deflagration phenomena

Factors affected by the rate of pressure increase in a given space and for a given amount of energy include: the pressure reached at equilibrium per unit amount of substance, and the reaction rate (or deflagration rate). The improved time/pressure test method is considered to be the test method that satisfies both constraints. In the case of having a clear flame front like $KClO_3$ /cellulose mixtures, the deflagration rate can be obtained by the method discussed above.

3.6 Pyrolytic Severity Test

3.6.1 Introduction

If an unstable substance or self−reactive substance in a tank or drum meets with a fire during storage or transportation, it begins to decompose with the heat conducted through the container. When the thermal decomposition is severe, an explosion or bursting may occur, causing damage.

The Keonen test [2, 37] , the Netherlands method [37, 46] and the American method [37, 47] for pressure vessel testing are known as test methods for evaluating fire dangers. For conventional methods for pressure vessel testing, refer to the previous book [1] where they are described in detail.

In Japan, the Fire Services Law(FSL) has recently been revised [101] and a pressure vessel test has been newly stipulated as the test method for determining the pyrolytic severity of Dangerous Goods− Class 5 Self−Reactive Substances−−set forth in the FPL [31] . In this section a description will be given of the procedure for pressure vessel testing set forth in the FPL and then our recent experience for pressure vessel testing.

3.6.2 Pressure vessel test (L): Classification test for FFL class 5 Dangerous Goods (Self-reactive substances)

1) Objective

The purpose of this test is to evaluate the pyrolytic severity of solid or liquid substances. For this purpose, the article under test is heated in a pressure vessel to examine if a bursting plate is ruptured at a probability of 50% when a prescribed orifice is used.

2) Test Method

(1) Test Apparatus

The test apparatus is composed of a pressure vessel and a heater, as shown in Fig. 3.73.

a) The pressure vessel is a stainless steel container with a capacity of 200 cm^3. It can hold a sample container, and an orifice plate and a bursting plate can be installed on the side and top, respectively, of the vessel.

b) The sample container is an aluminum cylinder about 30 mm in inside diameter, about 50 mm in height, and about 0.4 mm in thick with a flat bottom and an open top.

c) The orifice plates are made of stainless steel 2.0 mm thick. One Of these plates has an opening 1.0 mm in diameter and the other an opening 9.0 mm in diameter.

d) The bursting plate is a metal plate [*2] that will burst at a pressure of $(6.0 \pm 0.5)\mathrm{x}10^{5}$ Pa [*1].

e) The heater is an electric furnace with an output of 700 W or more.

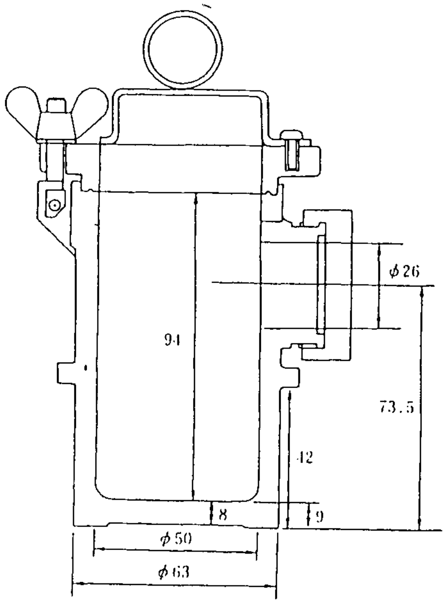


Fig. 3. 73 Cross-Sectional View of a Pressure Vessel (Netherlands Type)

(2) Test Procedure

a) Operate the electric furnace at the prescribed voltage and current [*3], and hold the condition for at least 30 minutes to pre–heat the furnace.

b) Install plate with an opening diameter of 9.0 mm on the side of the pressure vessel [*4], place the sample container containing 5 g of the test mterial on the center of its base, and install a bursting plate on the top of the vessel [*4].

c) Fill the bursting plate with water.

d) Place the pressure vessel in an electric furnace, and heat it until the bursting plate ruptures or the sample container temperature reaches 400 ℃ .

e) Repeat the operations from step c) to step d) 10 times.

f) If no rupturing occurs in at least 5 of the 10 test runs, replace the orifice plate with a plate 1.0 mm in opening diameter, and again perform the operation 10 times.

3)Interpretation of Results

The test material is classified according to the severity of pyrolysis as follows.

When rupturing occurs in at least 5 of the 10 test runs (50% probability) using an orifice plate 9.0 mm in opening diameter, the test material ranks I. It ranks II or III for 5 or more and 4 or less, respectively, of the 10 test runs using an orifice plate 1.0 mm in opening diameter.

<Foot Note>

*1 Expose the test apparatus to compressed air through the opening for orifice plate installation or other proper inlet, and measure the pressure at which the bursting plate ruptures.

*2 Aluminum or other suitable metal

*3 Set the voltage and current so that, when 5 g of silicone oil in a sample container is heated, the temperature of the sample rises at a rate of 40 ± 5 ℃ /min in the temperature range from 100 ℃ to 200 ℃ . Do not change this setting throughout the test.

*4 Use a heat resistant packing made of Teflon (polytetrafluoroethylene) or fluoro rubber.

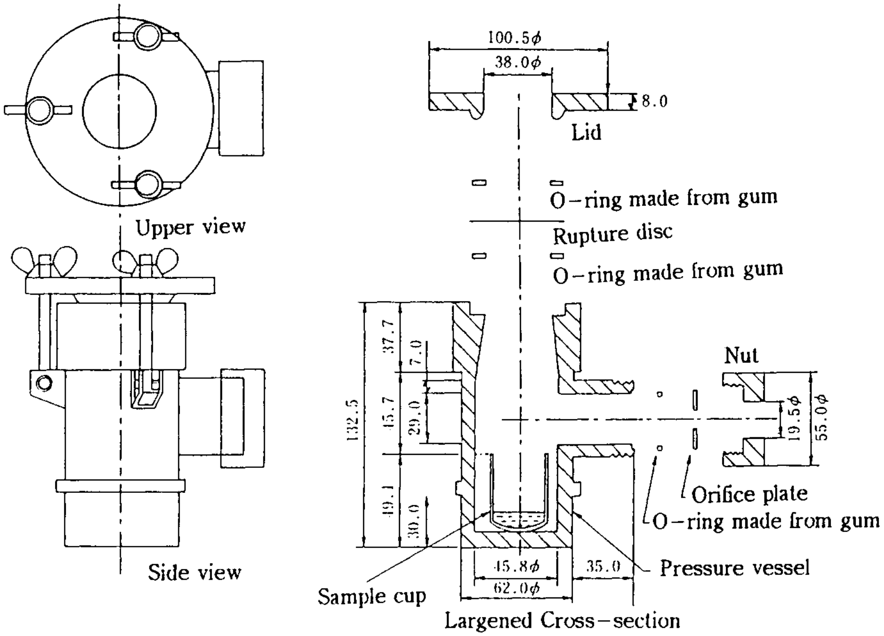


Fig 3.74 Pressure vessel installation in the Yoshida Lab of Tokyo University(US type)

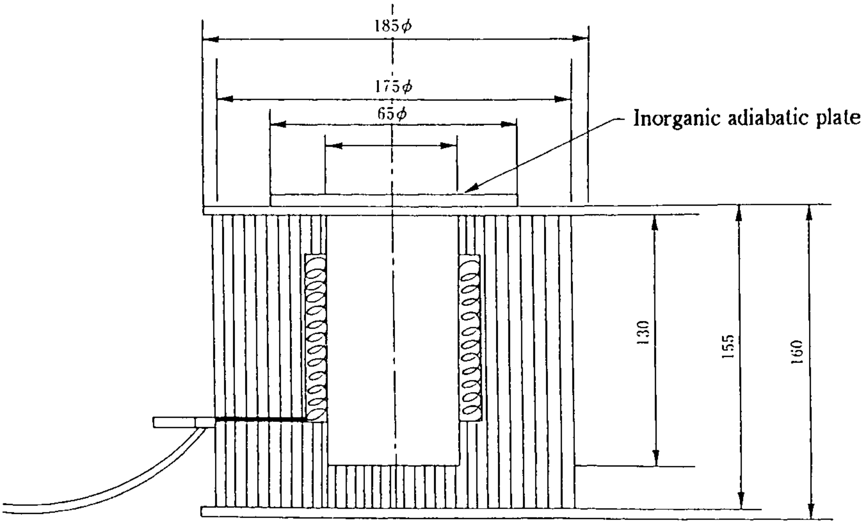
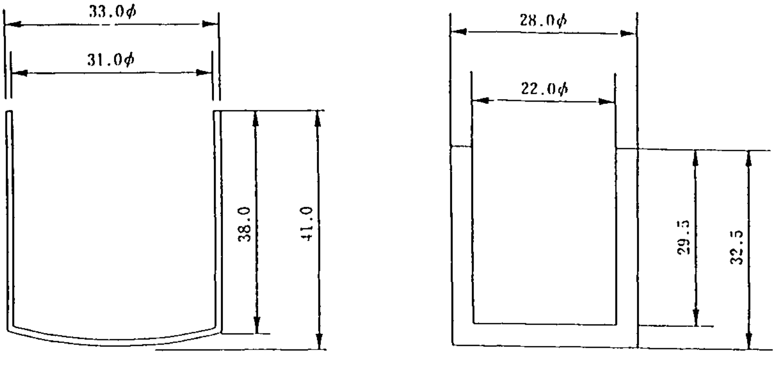


Fig. 3.75 Cross-section of electric heater in the Yoshida Lab of Tokyo University

3.6.3 Nature of the pressure vessel test

This section deals with the practical experience with pressure vessels of the American type in tests conducted in Professor Yoshida's Laboratory at the University of Tokyo, and the Gunpowder Research Laboratories of Nippon Oil & Fats Co.[48]



(a) (b)

Fig. 3. 76 Sample Cups
(a) Yoshida's Laboratory
(b) Nippon Oil and Fats Co.

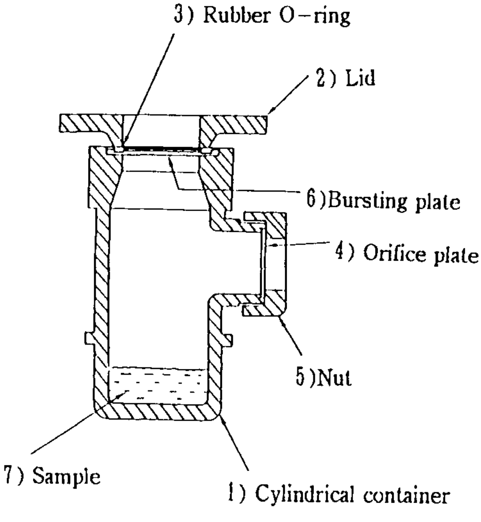


Fig. 3. 77 Sectional View of Pressure Vessel Test Apparatus (Nippon Oil and Fats Co.)

1) Pressure Vessels and Cups Used

The apparatus used at Yoshida's Laborayory is shown below.

The test apparatus is made of SUS type 316 stainless steel, and its lateral view and sectional view are given in Fig.3.74. An electric furnace with 8.4 Ω nichrome wire in which a voltmeter and an ammeter were installed is used for heating. The sectional view of the electric furnace is presented in Fig. 3.75. The supply voltage is adjusted by a 2-kW voltage regulator. The sample cup is shown in Fig.3.76 (a). It is made of aluminium and was an outside diameter of 33 mm, a thickness of 1 mm, and a height of 41 mm. The bursting plate is an aluminium disk 0.1 mm thick and 53 mm in diameter. The plate could be ruptured at a pressure of 6.0 ± 0.5 kg/cm^2 at ordinary temperature. Eighteen orifice plates with diameters of 1.0, 1.4, 2.0, 2.5, 3.0. 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10, 11, 12, 14, 16, 18, 20 mm are used. A heat-resistant packing made of BAITON is placed between the bursting plate and the orifice plate.

The test apparatus used at Nippon Oil and Fats Co. is as follows.

The specifications of the pressure vessel are the same as described by Noller et al [49]. The apparatus is shown in Fig. 3.77. The pressure vessel is a cylindrical container to which a bursting plate and an orifice plate can be installed. The orifice diameter is variable in 30 steps−−0, 1.0, 1.4, 1.7, 2.0, 2.4, 2.8, 3.5, 4.9, 5.9, 6.8, 7.6, 8.4, 9.0, 9.6, 10.2, 11.3, 12.3, 13.2, 14.0, 15.0, 16.2, 17.3, 18.2, 19.2, 20.0, 20.7, 21.8, 23.0, and 24.0 mm. All but the bursting plate and O−ring were made of SUS type 32 stainless steel. The bursting plate is made of aluminium 0.1 mm thick and 52 mm in diameter; the pressure at which it bursts is 9.75 ± 1.05 kg/cm^2 at ordinary temperature. Heating is carried out with a Teclu burner. The flow rate of fuel gas is adjusted so that a caloric value of 640 kcal/hr is obtained. A flow rate of 450 ml/min was suitable when propane gas is the fuel. The sample aluminium cup is shown in Fig. 3.76 (b).

2) Test Procedures (Yoshida's Laboratory)

(1) Conventional Method

Heat an electric furnace about 30 minutes before the test. Weigh 5 g of the sample into a cup, place it in a pressure vessel with an orifice plate, install a bursting plate, fill the bursting plate with water, and place the vessel, in the per−heated electric furnace. Record the presence or absence of rupturing of the bursting plate and the time required to decompose the sample. Upon completion of sample decomposition, record the time. Using protective gloves remove the pressure vessel from the electric furnace, and cool the vessel in water. Find the orifice diameter at which no rupturing occurs in three test runs. Perform the test in triplicate at the orifice diameter one size smaller than that diameter, and define, the orifice diameter at which bursting occurs at least once as the PVLD.

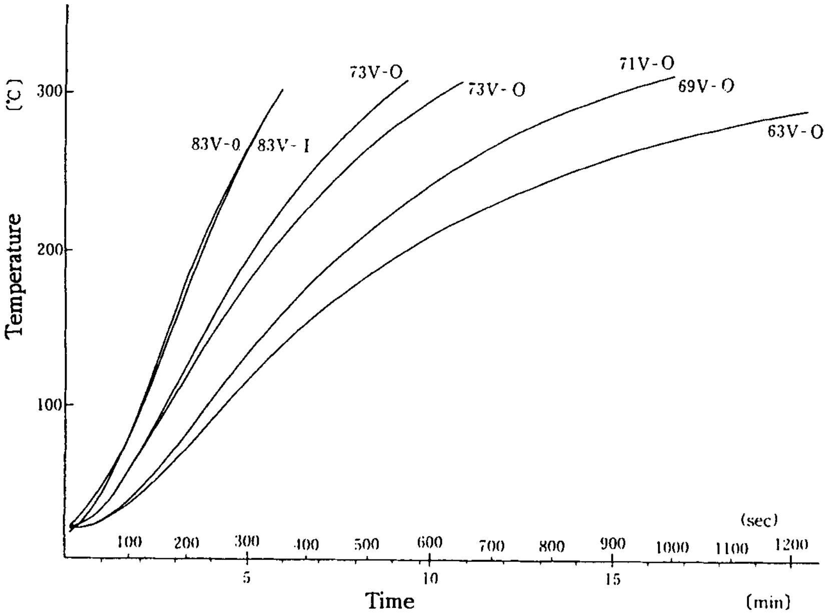
(2) 10−Run Method

Using orifice plates of 1 mm and 9 mm in diameter, perform the test 10 times for each sample, and record the number of burstings. The rest of the procedure is the same as for the conventional method.

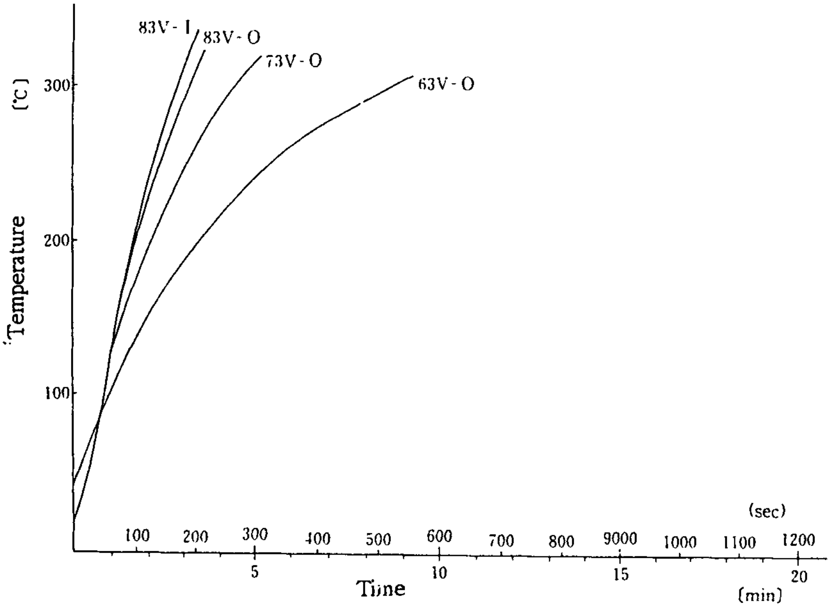
3) Test Procedure (Nippon Oil and Fats Co.)

Install an orifice plate of a proper diameter in a pressure vessel via an O−ring with box nuts. Weigh 5 g of the sample into an aluminum cup, place in the pressure vessel, and install a bursting plate on the vessel by putting it between two O−rings. Ignite a Teclu burner, and adjust the gas flow rate so that a caloric value of 640 kcal/hr is obtained. Check to see that the bursting plate is ruptured or the ejection of decomposed gas is complet. Continue testing until the minimum orifice diameter at which no rupturing occurs in two test runs is found.

4) Relationship between the Applied Voltage and Heating Rate

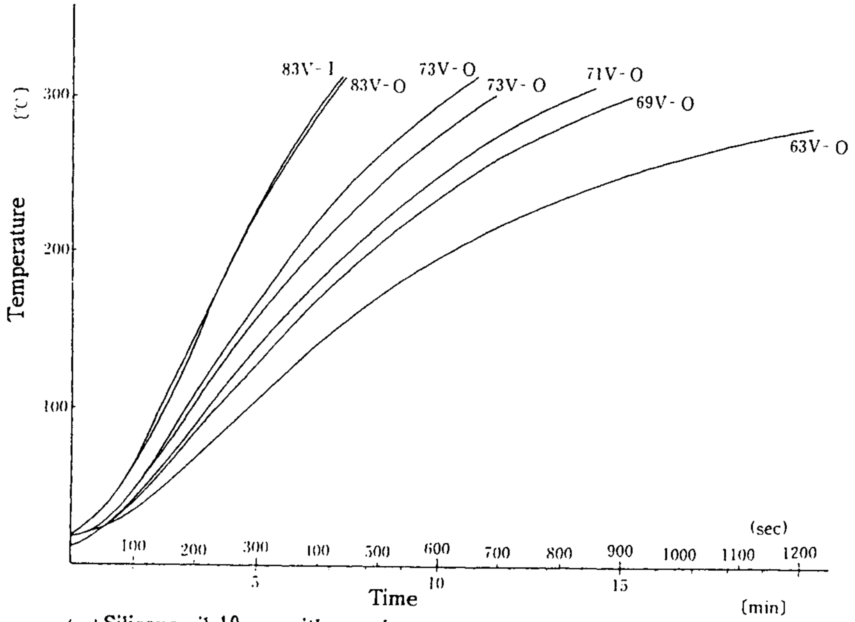


(a) Silicone oil 5 g, with sample cup

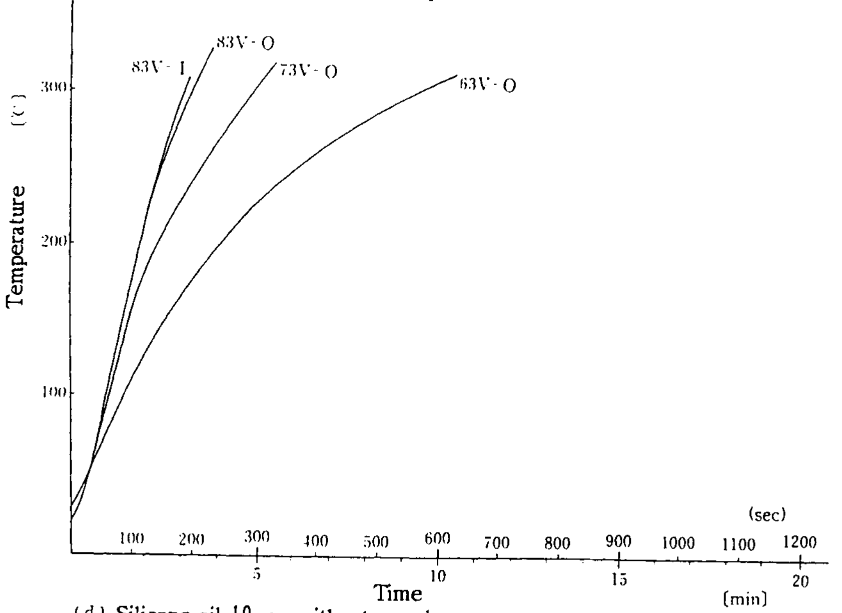


(b) Silicone oil 5 g, without sample cup

Fig. 3.78 Rate of temperature increase of the pressure vessel



(c) Silicone oil 10 g, with sample cup



(d) Silicone oil 10 g, without sample cup

O – Outside I – Inside

Fig. 3.78 Rate of temperature increase of the pressure vessel(continued)

Five g and 10 g of silicone oil are placed in the bottom of a pressure vessel and a cup, respectively, and the silicone oil temperatures are measured with a thermocouple. The results are shown in Fig. 3.78 (a)−(d). The mean heating rate determined from 100 to 200 ℃ is defined as the heating rate; valices are summarized in Table 3.32. The rate was plotted against the voltage applied to the electric furnace and is presented in Fig. 3.79. This test was conducted indoors and outdoors, and no difference in the heating rate was seen.

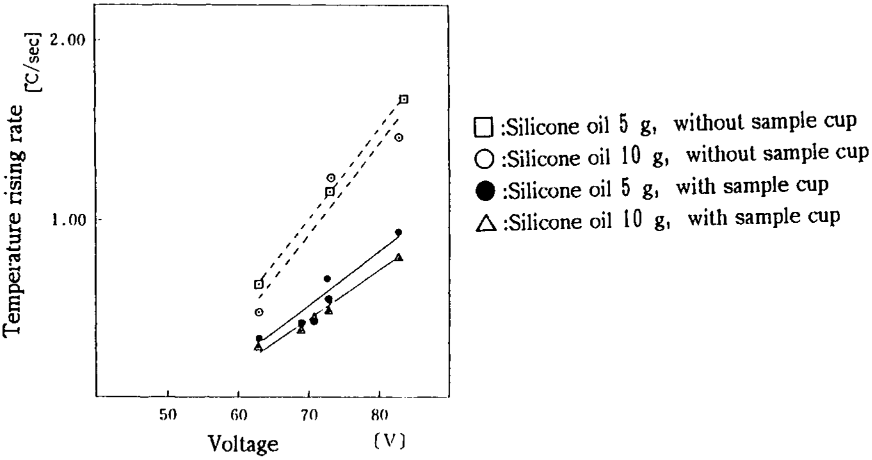


Fig 3.79 Rlation between loading voltage and rate of temperature increase in the electric heater of pressure vessel

5) Effects of the Presence of a Cup

The difference in heating rate in the presence and absence of a sample cup is considerable at the same applied voltage. As shown in Table 3.33, results of three tests by the Nippon Oil and Fats Co. method show that the PVLD was larger in the presence of a cup than in the absence.

Table 3.32 The relationship of the loading voltages of the heater in the pressure vessel and heating rates

Voltage [V]	Current [A]	Heating rate(℃/sec)							
		with cup				without cup			
		outside		inside		outside		inside	
		5g	10g	5g	10g	5g	10g	5g	10g
63	7.6	0.34	0.3			0.65	0.48		
69	8.2	0.43	0.40						
71	8.5	0.43	0.44						
73	8.8	0.57	0.50			1.15	1.24		
73	8.8	0.67	0.58						
83	9.9	0.95	0.80	0.95	0.85	1.67	1.47	1.89	1.47

Table 3.33 The effect of the aluminium cup

Heating rate:0.5 ℃ /sec, Sample mass:5g, Nippon Oil and Fat Co.

Substances	UN No.	PVLD (mm)	
		with cup	without cup
t-Butyl peroxybenzoate	2097	8.4	4.9
Di-t-butyl peroxide	2102	1.0	<1.0
55% Methylethylketoneperoxide Dimethylphthalate solution (active oxygen 10.3%)	2127	2.3	<1.0

6) Effects of the Amount of Sample

Effects of the amount of sample are shown in Table 3.34. There is no particular trend in effects of the amount of sample on the PVLD. Although 5 g and 10 g of sample were used, the amount of sample does not greatly influence the PVLD. Five g of sample is recommended with safety in mind.

Table 3.34 The effects of sample mass on heating rate

Substances	UN No.	Mass (g)	PVLD (mm) Heating rate	
			0.5～0.7℃/s	～1.0℃/s
t-Butyl peroxybenzoate	2097	5	3.0	6.0
				3.0
		10	3.0	3.0
				4.0
Di-t-butyl peroxide	2102	5	<1.0	<1.0
		10	<1.0	<1.0
55% Methylethylketone peroxide and Dimethylphthalate solution	2127	5	10	4.0
				3.0
		10	6.0	3.0
				6.0

Heating rate:0.5 ℃ /sec, without cup, Nippon Oil & Fat Co.

Substances	UN No.	PVLD (mm)	
		Mass 5g	Mass 10g
t-Butyl peroxybenzoate	2097	4.9	6.8
Di-t-butyl peroxide	2102	<1.0	<1.0

7) Effects of the Heating Rate

As shown in Table 3.34 for effects of the heating rate on PVLD, no relationship between the temperature rise rate and PVLD is seen.

8) Results of 10−Run Tests at Yoshida's Laboratory

Results of pressure vessel tests using either a 1 or a 9 mm diameter orifice plate are summarized in Table 3.35. In this instance, the applied voltage is 73 V and the heating rate is about 0.5 ℃ /sec in the range from 100 to 200 ℃ .

Bursting occurred at an orifice diameter of 1 mm in 9 of 10 test runs for 80% AIBN−20% α $-Al_2O_3$, whereas no bursting occurred at a diameter of 9 mm in 10 runs for 70% AIBN−30% α $-Al_2O_3$.

9) Comparison of Test Data

A comparison of these test data and those in the textbook from the First United Nations Seminar on Organic Peroxides is presented in Table 3.36. Except for di−t−butyl peroxide, PVLD showed great variation in the various tests.

10) Precision and Reliability of the Pressure Vessel Test

Results of this study indicate wide variations in data. The PVLD varied with the manufacturing lot of methyl ethyl ketone peroxide, and the same was true for t−butyl benzoate.

11) Improvement in the Pressure Vessel Test

Despite data on the conventional test for pressure vessels showing much variation, the test is considered effective in determining the pyrolytic severity of unstable substances including organic peroxides.

Table 3.35 Results of pressure vessel test using plates with orifice diameters of 1 mm and 9 mm

Samples	AIBN			BPO		
Concentration	90%	80%	70%	80%	70%	60%
Orifice Diameter		1 mm			9 mm	
Test No.						
1	○	○	×	○	×	×
2	○	○	×	○	×	×
3	○	○	×	○	×	×
4	○	×	×	○	×	×
5	○	○	×	○	×	×
6	○	○	×	○	×	×
7	○	○	×	○	×	×
8	○	○	×	○	×	×
9	○	○	×	○	×	×
10	○	○	×	○	×	×
Results	10/10	9/10	0/10	10/10	0/10	0/10

○ Rupture, × No rupture.

The rupture ratio of ADCA is 4/10 using the 1mm orifice plate(Yoshida Lab); data obtained in the Nippon Carlit Co. yields a ratio of 1/10, and maxmium pressure is 5.4

kg/cm^2 50).

Table 3.36 Comparison of limit diameters of pressure vessel tests

Substances	UN No.	Mass	PVLD (mm)						
			Heating rate (℃/sec)						
		(g)	0.5-0.7[a]	1.0[a]	0.5[b]	0.5[c]	0.5[d]	1.0[e]	0.5[e]
t-Butyl peroxybenzoate	2097	5	3.0	6.0	8.4	4.9			10
				3.0					
		10	3.0	3.0		6.8		9.0	
				4.0					
Di-t-butyl peroxide	2102	5	<1.0	<1.0	1.0	<1.0	<1.0		1.0
		10	<1.0	<1.0		<1.0		3.5	
55% Methyl ethylketone peroxide Dimethyl phthalate solution	2127	5	10	4.0	2.3	<1.0	3.5		
				3.0					
		10	6.0	3.0					
				6.0					

a:Yoshida Lab, with cup,
b:Nippon Oil & Fat Co., with cup,
c:Nippon Oil & Fat Co., without cup,
d:Added data, Nippon Oil & Fat Co., without cup,
e:ref.(4)

There is a problem in the conventional method in that the orifice diameter intervals are narrow. Classifying the pyrolytic severity in 10 or more steps is considered impractical. When the orifice diameter is broadened by decreasing the number of orifices, consistent data will be obtained.

3.7 Shock Sensitivity Test

3.7.1 Introduction

Explosion often occurs as a result of a blow or shock. Impact sensitivity is shown by the tendency of a substance to explode from a blow, and the shock sensitivity is shown by the tendency to explode from a shock. It is important to distinguish between both kinds of sensitivity.

The drop hammer test was the most popular sensitivity test for explosives, but some problems existed with this evaluation. First, the range of sensitivity in this test is narrow; therefore the sensitivity of many explosive materials or materials which have the potential to explode cannot be evaluated. Highly sensitive materials could not be distinguished because neither high now low sensitivity explosive materials could be completely evaluated.

As a countermeasure a modified method is to dilute the material with hard sand or to use sand emery paper, but these methods are not always effective. Furthermore, a heavy weight drop hammer must be used. This is not a useful test because it is difficult to maintain the equipment.

Because of the problems with blow and shock sensitivity tests, we sought to develop new test methods. The rank of the sensitivity of explosive substances has been determined by combining the methods shown in Table 3.37.

Table 3.37 Practical impact · shock sensitivity tests

Testing materials	Test methos
Very high sensitivity	Drop ball impact sensitivity test
High sensitivity	Drop ball impact sensitivity test Small gap test
Medium sensitivity	(Small gap test) Variable initiator test
Low sensitivity	Variable initiator test 50/60 steel tube test

Examples of very highly sensitive substances are mixture of chlorates–red phosphorus, paper cracker, lead azide, and DDNP. High sensitivity substances are dynamite(powder), PETN(powder), HMX(powder), RDX(powder), tetryl(powder), picric acid(powder), TNT(powder), and benzoyl peroxide (powder). Medium–sensitivity substances are the modern safety industrial explosives (slurry explosives, ammonium nitrate explosives), black powder, AIBN, and t–butyl–benzoate. Among low sensitivity substances are non–cap explosives: dinitro benzene, dinitropentamethylenetetramine, ANFO, ammonium nitrate, nitromethane, dinitrotoluene, and cast TNT.

3.7.2 The variable initiator test by using the MKIII ballistic mortar(M) [27]

M1. Name of test

The variable initiator test using the MKIII ballistic mortar.

M2. Property evaluated

Shock sensitivity of explosive substances with low or medium sensitivity.

M3. Equipment and materials

The outline and the cross section of the revised MKIII ballistic mortar are shown in Fig

3.80. The sample assembly and the projectile are contained in the bore of the mortar that is 229mm long with an internal diameter of 25mm, flaring out at the open end to form a venturi. The mortar is suspended by four stainless steel cables 188mm in external diameter, and 457mm long that allow it to swing freely. The total weight is approximately 110kg, and the suspension length is 2080mm.

The cross section of the projectile made of soft steel is shown in Fig 3.81. The entire experimental assembly and its parts for the variable initiator test are shown in Fig 3.82. The glass sample tube is a 10 or 15 ml commercial one. The size of the tube is selected according to the density of the sample.

A No.0 or No.6 detonator is used as the initiator. The PETN is in the form of pure and fine dry crystals.

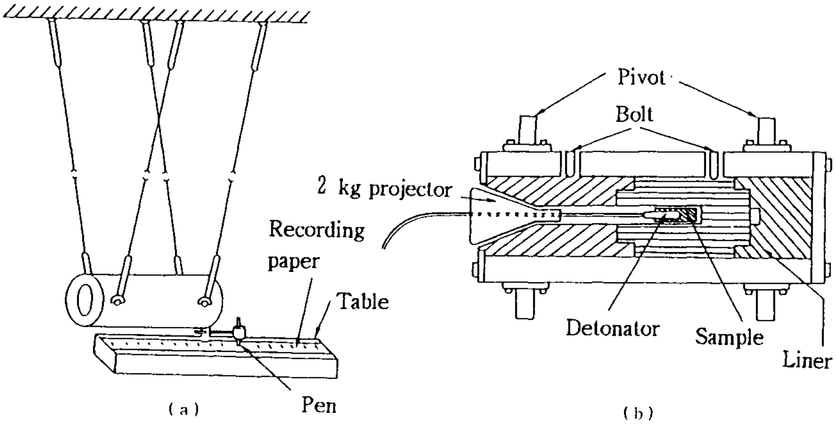


Fig 3.80 Appearanee(a) and Cross−section(b) of modified MK III ballistic mortar

M4. Procedure

This test is not done when the drop hammer test or the small gap test indicated high sensitivity on the part of the tested substance. A 5.0 g sample of the substance is placed in a 10 or 15ml sample tube. If the density of the substance is high, 10 ml sample tube is used to avoid a space between the substance and the inner polyethylene tube. A polyethlene lid with a hole is attached to the sample tube.

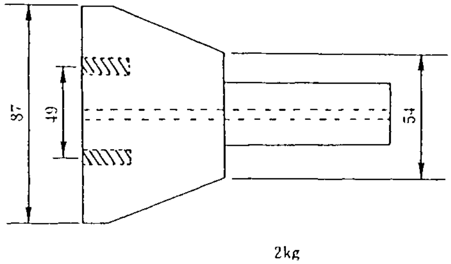


Fig. 3.81 Cross−section of projector

A 0.1 ~ 0.6g sample of PETN is weighed in the inner tube. Fov a No.0 detonator frce maximum weight of sample is 0.3g.

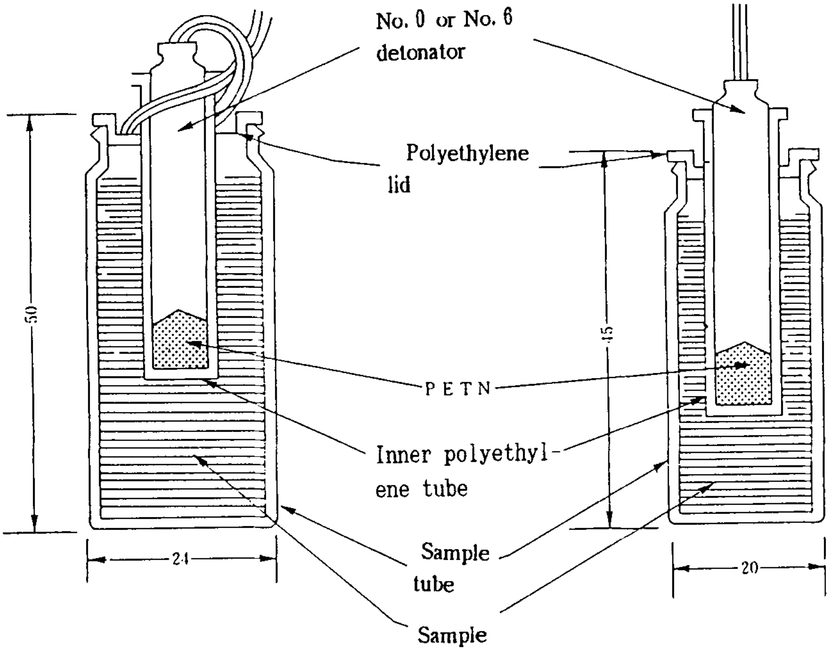


Fig. 3.82 Cross-section of sample insert

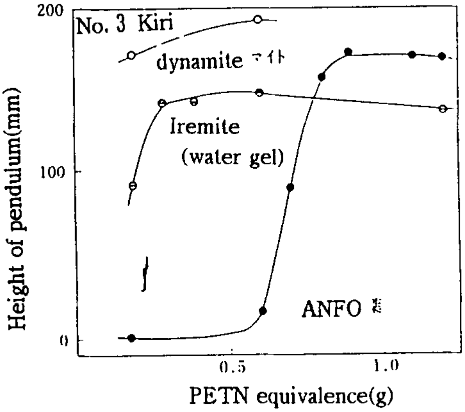


Fig.3.83 Height of pendulem for industrial explosives

The inner tube is inserted through a hole in the lid into the substance in the sample tube. A No.0 or No.6 detonator is inserted into the inner tube and fixed to the tube by winding the leg wires.

The test sample assembly is inserted into the bore of the mortar and the projectile is attached to the open end of the mortar. A pen is inserted into the hole in the pen-holder and a reference line is marked on the strip chart paper when the fully-loaded mortar is at rest. The detonator leg wires are connected to the firing circuit and the charge is fired. The pendulum swing length can be read from the results recorded on the strip chart paper.

M5. Evaluation of the results

The net swing length is calculated from the displacement of the ballistic mortar. Here, the net swing length is the difference between the swing length for the explosion of the substance plus initiator and that of the initiator alone. The net swing length obtained is plotted against the PETN equivalence and a curve for the net swing length is drawn. The PETN equivalence of the initiator is the weight of PETN (g) obtained from the swing length of the mortar equivalent to the initiator (detonator + PETN). Curves of the net swing length for the typical industrial explosives are shown in Fig 3.83.

M6. Criteria for the test

High sensitivity : 5g of the substance is exploded completely by a No.0 detonator.

Medium sensitivity: 5g of the substance is exploded completely by a No.6 detonator but is not exploded by a No.0 detonator.

Low sensitivity : 5g of the substance is not exploded by a No.6 detonator.

The complete detonation of 5g of the substance occurs if the curve of the net swing length displays saturation. The relative sensitivity is judged by the position of the net swing length at saturation. The further to the right the saturation, the more sensitive the material.

3.7.3 The small gap test by using MKIII ballistic mortar (N) [28]

N1. Name of test

The small gap test using MKIII ballistic mortar.

N2. Property evaluated

Shock sensitivity of relatively high sensitivity explosive materials.

N3. Equipment and materials

The equipment is the same MKIII ballistic mortar used in the variable initiator test. The sample assembly for the small gap test is shown in Fig 3.84. A No.0 detonator is used.

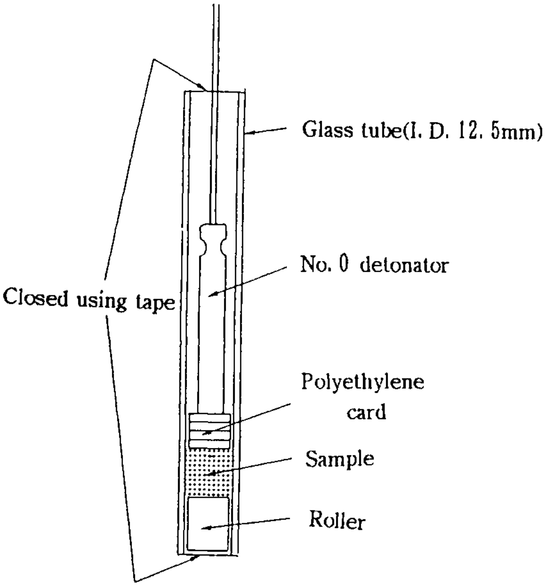


Fig. 3.84 Sample set-up for the small scale gap test

N4. Procedure

The steel cylinder is inserted into the tube and fixed by an adhesive tape at the open end of the glass tube. One gram of the substance is poured into the tube, and polyethylene cards 1 or 2 mm thick are wrapped with an adhesive tape, and placed on the substance and pressed softly. A No.0 detonator is inserted into the tube and fixed until the bottom of the detonator touches the top of the cards. The procedure after the sample assembly is inserted is the same as the procedure in the variable initiator test.

N5. Evaluation of the results

The net swing length per g is calculated when the swing length by No.0 detonator (9mm) is subtracted from the swing length of the mortar; the value multiplied by 5 is the net swing length per 5 g of sample. The logarithm of the thickness of the cards (the gap length) on the X–axis is plotted against the net swing length per 5 g os sample on the Y–axis, and the curve describing the net swing length in the small gap test is determined. The curves for typical explosive compounds are shown in Fig 3.85.

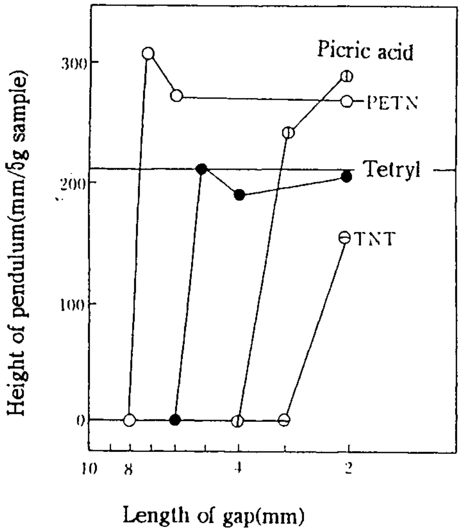


Fig. 3.85 Height of the pendulum for high explosives in the small scale gap test

N6. Criteria for the test

Very high sensitivity : The net swing length is greater than 20mm at an 8 mm gap for 5.0g of the substance.

High sensitivity : The net swing length is less than 20mm at an 8mm gap and is greater than 20mm

at a 2mm gap for 5.0g of the substance.
The relative sensitivity is judged by the position of the curve; the further to the left the curve, the more sensitive the material.

3.7.4. Applied example of the shock sensitivity test using the MKIII ballistic mortar 53, 54)

(1) Indication of sensitivity by the small gap test and the variable initiator test

The shock sensitivity of explosive substances can be examine over a wide range by combining the small gap test and the variable initiator test. The results of the two experiments can be shown in one diagram. Although this procedure may not be based on rigorous theory, we show the results of its application in Fig.3.86.
The horizontal axis is the a logarithm of the gap length in the small gap test and the PETN equivalent in the variable initiator test. The vertical axis is the net length of the swing of the mortar per 5 grams of sample. The examples graphed in Fig 3.86 are PETN and m−Dinitrobenzen(m−DNB). PETN is a fairly sensitive substance, and it has been suggested that substances that the transport of substances more sensitive than PETN should be forbidden. Though DNB is an explosive which can be detonated by a strong initiation, it is a relatively insensitive substance. A substance which is less sensitive than DNB is a low−sensitivity substance. An examination of data shows that the sensitivity of DNB is almost the same as ANFO.
The further the maximum value of the net length of swing lies to the left, the more sensitive the substance.

(2) Explosive Compound

The sensitivity ranking is PETN > RDX Tetryl > Picric acid > TNT. Other substances are shown in Fig.3.86. In comparison with Fig3.85 and Fig.3.87, the sensitivity of Pentalite seems to be almost equal to that of picric acid. Pentalite is a 1:1 mixture of PETN and TNT by weight and its sensitivity is halfway between that of PETN and TNT. The sensitivity of DNT (2,4−dinitrotoluene) is lower than DNB. We are unable to comment on the sensitivity of HMX and NC as we did not conduct the small gap test on these substances. Fig.3.88 shows the net swing curves for TNT and nitromethane. TNT is a solid substance at room temperature; its sensitivity is high when it is powdered and low when it is cast. Nitromethane is a liquid at room temperature. Nitromethane by itself is relatively insensitive, but it becomes highly sensitive when (glass micro spheres) are mixed with it. At this stage, however, we have not examined liquid substances in the small gap test. Since explosive substances can be more sensitive when air bubbles are contained within, one must be extremely careful when handling them.

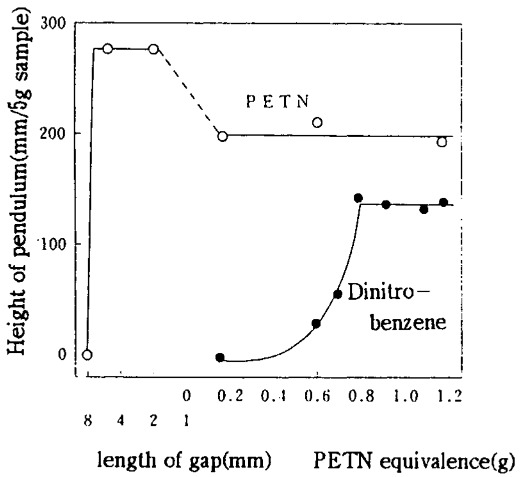


Fig. 3.86 Display of the sensitivity of the small scale gap test and the variable ignitor test(e.g.PETN & DNB) 54)

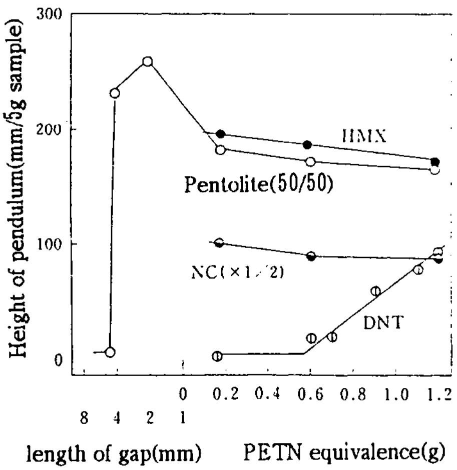


Fig. 3.87 Height of pendulum for Pentolite, HMX, NC and DNT 54)

(3) Unstable Compound

Fig.3.89 shows the net length of the swing of compounds with unstable atomic groups. The explosive power of DPT and AIBN is not very large, but 5 grams of the sample substances exploded completely where more initiators was used. According to another examination, it is clear that DPT and AIBN can continue to explode and to propagate an explosion. Both of these compounds have caused explosive accidents in the past. AIBN seems to be a limited explosive that can sustain propagation with one−fourth the explosive static power of TNT. This propagation of detonation seems to be possible because it is comparativly sensitive. In a range of experiments, nitropropane did not dermonstrate an explosive reaction even with the maximum initial explosive quantity. Nitropropane has almost same amount of decomposition energy as DNT according to calculations, but it is considered to be difficult to explode. An experiment including air bubbles should be carried out to confirm this.

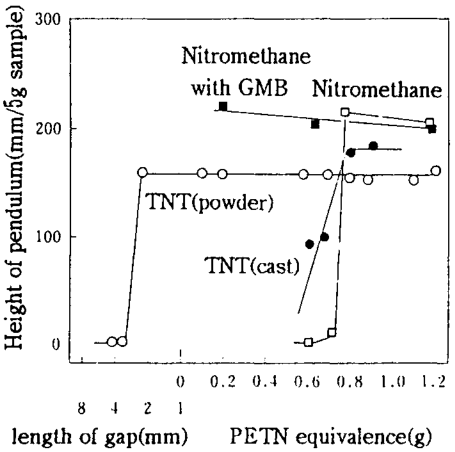


Fig. 3.88 Height of pendulum for powdered TNT, cast TNT, nitromethane and nitromethane with glass micrispheres

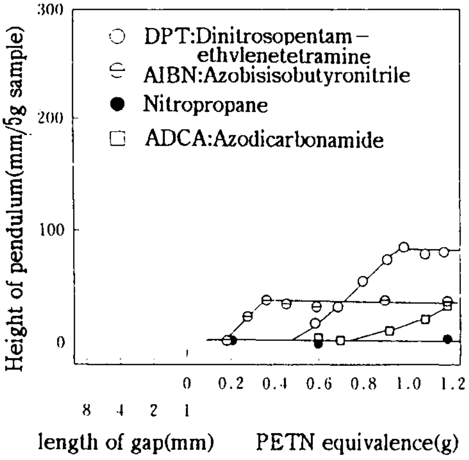


Fig. 3.89 Height of pendulum for DPT, AIBN, ADCA and nitropropane

ADCA is a dangerous substance and was treated as a dangerous material for transport by ship, but it has been taken off the dangerous goods list. According to the variable initiator test, it is less sensitive than DPT. When a large amount of initiator is applied, it decomposes slightly around the initiator, but it has been confirmed that it does not propagate an explosion in the 50/60 steel tube test. It can be regardedas safe with regard to an explosion hazard.

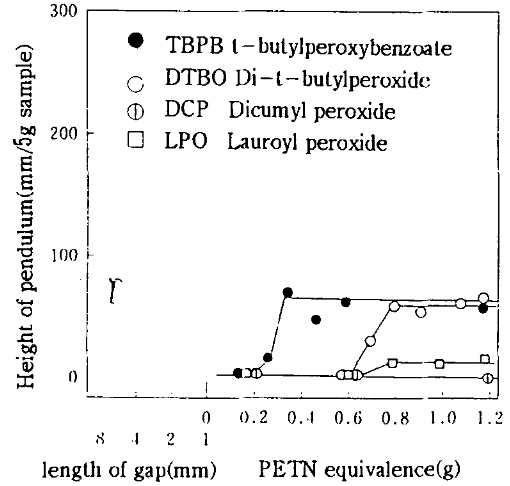


Fig. 3.90 Height of pendulum for organic peroxides(I)

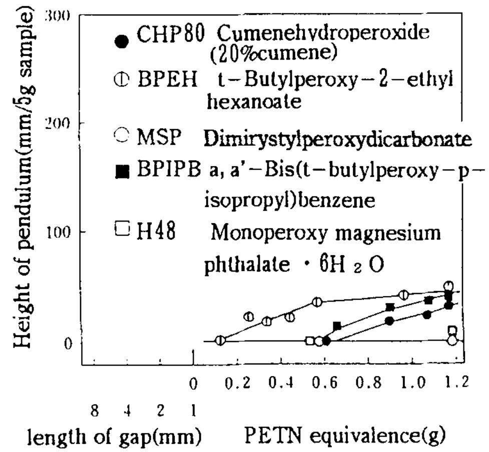


Fig. 3.91 Height of pendulum for organic peroxides (II)

(4) Organic Peroxides [55, 56]

There is a group organic peroxides used in pharmaceuticals which have unstable chemical structures. They were produced by Nippon Oil and Fats Co., Ltd. and Kayaku

Noury Co., Ltd. which is one of the Nippon Kayaku Co., Ltd. Group, because of their experience with the safe manufacture of explosives. Fig.3.90 shows the net length of swing of four kinds of organic peroxides. TBPB and DTBO propagate explosions, but DTBO seems to be a limiting substance because its sensitivity is low. Five grams of LPO explodes completely if the PETN equivalent is more than 0.8 g, but it did not propagate an explosion. DCP does not decompose explosively. Fig.3.91 shows the net swing length of five other substances, and Fig.3.92 shows that of benzoylperoxide(BPO). The range of sensitivity of BPO as a function of added water was also examined. Pure BPO is a highly sensitive substance, and as its water content increases, it becomes less sensitive. In other experiments, 80% BPO (20% water content) is found to propagate an explosion, but 75% (25% water) does not. Benzoylperoxide has been the cause of many accidents because of its extreme sensitivity. The results of this test have established that its explosion hazard can be diminished by the addition of water.

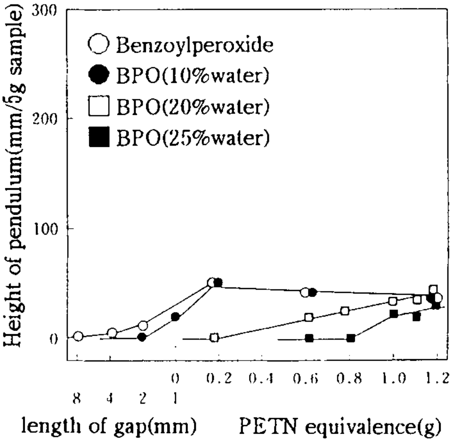


Fig. 3.92 height of pendulum for Benzoylperoxide

(5) Mixtures of oxidizers

Fig.3.93 shows the data on the sensitivity of ammonium nitrate, which is an important explosive material. There is a difference in the sensitivity level between crystalline and prilled ammonium nitrate (AN (Prill)), which has many holes in the porous grains that make it more sensitive. The porous prills do not explode completely at a PETN equivalent 1.2g, but they do in the 50/60 steel tube test with an initial explosive booster of 50 g of RDX.

ANFO is a mixture of AN (Prill) : fuel oil (94:6), and it explodes completely with a PETN equivalent of 0.8g initiator. We had to be extremely careful when collecting the data for Fig. 3.93. In the experiment on the oxidizer alone, the polyethylene inner tube, used as a untainer for the initiator may react with the oxidizer. This seems to be the reason why the explosive power of prilled AN is as large as that of ANFO in the experiment with 1.1g PETN equivalence.

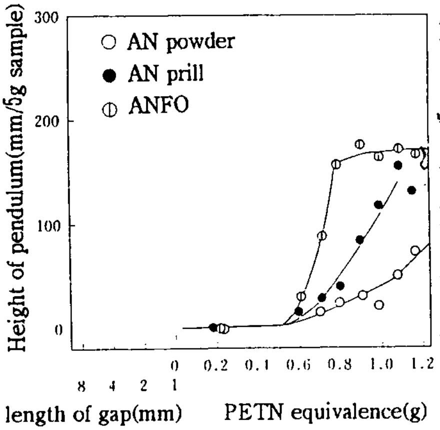


Fig. 3.93 Height of pendulum for AN powder AN prill and ANFO

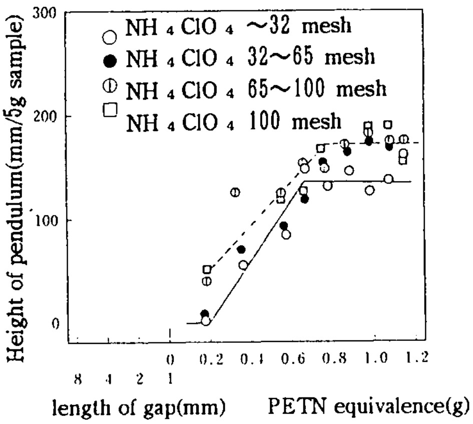


Fig. 3.94 Height of pendulum for NH_4ClO_4

Fig.3.94 shows the curves of the net swing length of ammonium perchlorate (AP), which is a material used in composite propellants and carlit explosives. A small difference in sensitivity is shown as afunction of particle size, the smaller sizes of AP having of higher sensitivity . The explosive power of the smaller sizes is observably larger and may be due to reaction with the polyethylene inner tube.

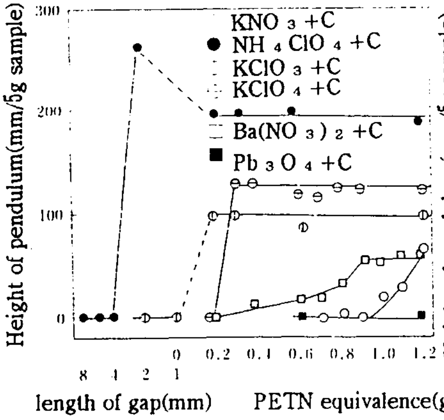


Fig. 3.95 Height of pendulum for mixtures of oxidizers with charcoal

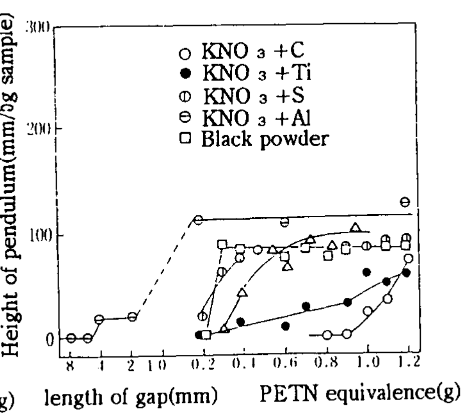


Fig. 3.96 Height of pendulum for mixtures of KNO_3 with combustibles

Fig.3.95 shows the net swing curves for stoichiometric mixtures of oxidizers and hemp charcoal. Generally, when oxidizers and combustible substances are mixed, the mixtures becomes more sensitive. Fig 3.95 shows the results of the experiment to establish which oxidizers make highly sensitive mixtures, using hemp charcoal as the combustible substance. The order of sensitivity of the oxidizers is :

ammonium perchlorate > potassium chlorate > potassium perchlorate > barium nitrate > potassium nitrate > red lead

According to this experimental result, ammonium perchlorate is a rather dangerous oxidizer. However, composite propellant containing ammonium perchlorate, does not propagate an explosion. After treatment, ammonium perchlorate may be safer to handle. Fig.3.96 shows the curves of the net swing length of mixture of potassium nitrate and various combustible substances. The order of the sensitivity of the mixtures of the combustible substances and potassium nitrate is (red phosphorus) > aluminium > sulfur > titanium > hemp charcoal.

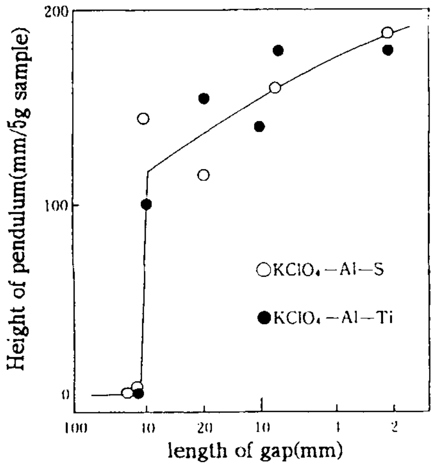


Fig. 3.97 Results of small scale gap test for mixtures of KClO4 − Al series

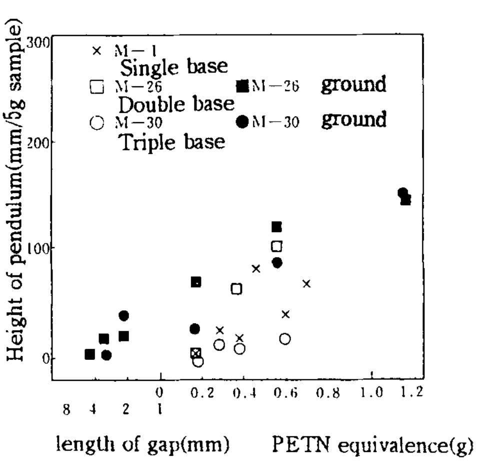


Fig 3.98 Height of pendulum for the smokeless powder series

Aluminium enhances the sensitivity of the oxidizer.

Aluminium, which is used for water gel explosives, behaves as a sensitizer. Fig.3.97 shows the results of experiments with potassium perchlorate − aluminium powder − sulfur and potassium perchlorate − aluminium powder − titanium powder. According to these results it seems that the mixture of potassium perchlorate − aluminium powder is a highly sensitive substance.

Very high sensitivity substances like this should not usually be examined in the small gap test which requires 1g of a sample. This type of substance should be evaluated by the drop ball test.

In this case, the sensitivity is almost the same even if the third ingredient is titanium or sulfur. The sensitivity of the mixture depends on the combination of highly sensitive substances. Fig.3.96 also shows the curve of the net swing length for black powder. This curve is similar to that of potassium nitrate – sulfur. The sensitivity of black powder is that of a high ignitability substance. Once it is ignited the fire encompasses the grain, then it explodes. This is the reason why there are no data about partial reaction in the curve.

(6) Smokeless gun powder 58)

The experiment with the MKIII ballistic mortar were run on smokeless powder because the powder is a problem to transport. there are three kinds of smokeless gun powder: single base gun powder, double base gun powder and triple base gun powder.

Gun powder is also molded into several shapes. The scatter in the results from the examination of gun powder is shown in Fig. 3.98. The scatter results from the difficulty in making the test samples the same shape. Initial experiments gave an order of sensitivity of triple base < single base < double base. However, when the grains of powder were broken into smaller fragments and retested, the overall sensitivity increased and the order was single base < triple < double base. The sensitivity of gun powder depends not only on its composition by on the shape of the grains.

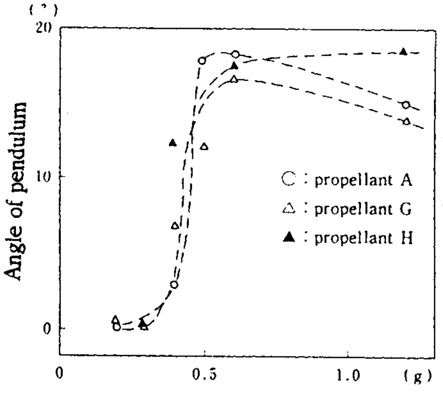


Fig. 3.99 Angle of pendulum for composite propellant(I)(ballistic mortar in Nippon Oil & Fat Co.)

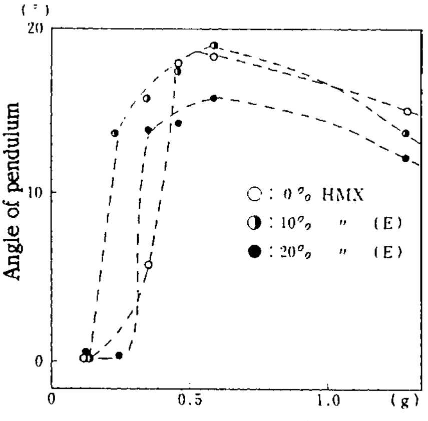


Fig. 3.100 Angle of pendulum for composite propellant(II)(ballistic mortar in Nippon Oil & Fat Co.)

(7) Composite Rocket Propellant 59-61)

Fig.3.99 ~ 3.101 show the results of the variable initiator tests on composite propellants. Table 3.38 shows the formulation of the propellants used in these experiments. Propellants were kneaded and cured in a vacuum in order to eliminate bubbles. In this experiment the amount of reagent is large (about 15g) so the MKIII ballistic mortar could not be used, but the conventional type ballistic mortar of the Nippon Oil and Fats Co.,Ltd. Taketoyo Factory was used. This experiment shows how explosive properties change when HMX is added to composite rocket propellants. According to the diagram, the sensitivities are not changed much if HMX is added. In spite of a combination of ammonium perchlorate and aluminium powder, the sensitivity is not high. The most important factor is that this combination is hardened by a gummy substance, HTPB, and is degasified. Its, sensitivity is altered by its physical condition. In this experiment, composite propellants are exploded completely by a No.6 detonator. However, in the other experiment, these propellants (except composition C) did not propagate an explosion.

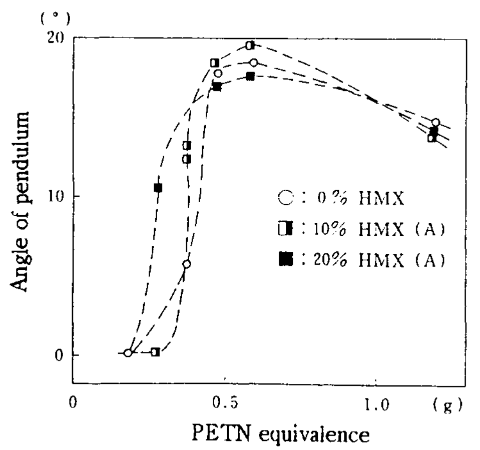


Fig. 3.101 Angle of pendulum for composite propellant(III) (ballistic motar in Nippon Oil & Fat Co.)

Table 3.38 Composition of composite propellants(wt.%)

Mark	HTPB	Al	NH_4ClO_4	HMX(A)	HMX(E)
A	11	18	71	0	0
B	11	18	61	0	10
C	11	18	51	0	20
D	11	18	61	10	0
E	11	18	51	20	0
F	11	18	41	30	0
G	12	18	62	0	8
H	14	18	68	0	0

HMX(A): mean diameter of particles 200 μ m,
HMX(E): mean diameter of particles 20 μ m,
HTPB: fuel binder.

Explosive substances usually propagate an explosion if 5g of the substances explode completely in the MKIII ballistic mortar. The same phenomenon is not observed with composite propellant. Regarding this point, the 50/60 steel tube test in water can give precise information about detonation propagation. We now know that composite propellant is difficult to detonate. When it is initiated using the MKIII ballistic mortar with a No.0 detonator, it does not show any explosive power but bursts into flame and starts to burn. In short, self-sustained explosion is hard to produce, but ignition occurs easily. In this respect composite propellant is different from industrial explosives, ANFO and slurry explosives.

(8) Industrial Explosives [64]

The results of shock sensitivity tests on industrial explosives by the small gap tests and variable initiator tests are shown in Fig 3.102. In the range of experiments the shock sensitivity turns out to be smaller. They are listed in order of their sensitivity as follows: No.2 Enoki Dynamite, No.3 Kiri Dynamite, Energel MA-7, No.5 Black Carlit, Akatsuki Carlit, Iremite, Hamamite, and ANFO.

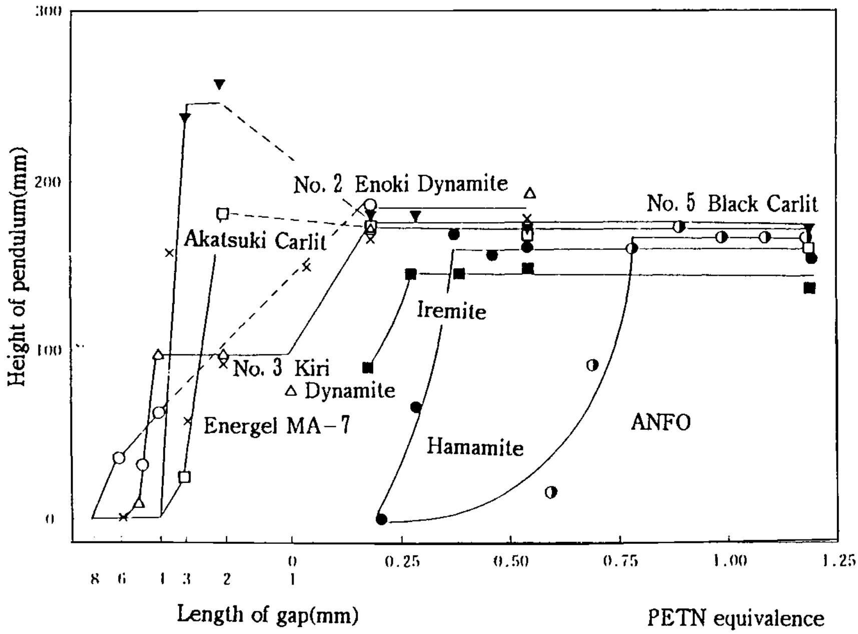


Fig. 3.102 Results of shock sensitivity test for industrial explosives

3.7.5 Properties of the MKIII ballistic mortar

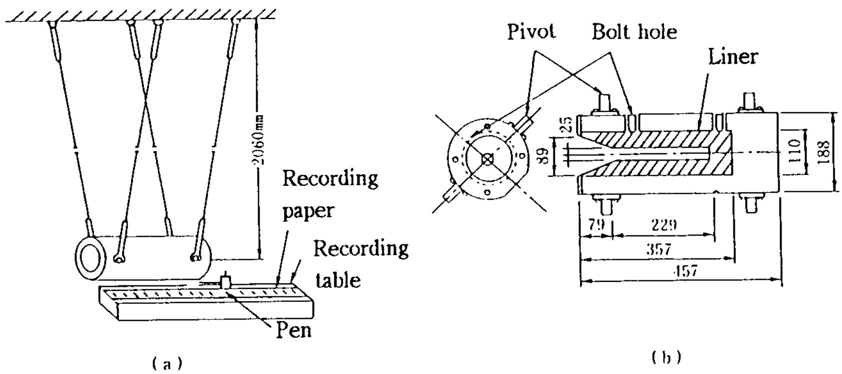
(1) Ballistic mortar

The ballistic mortar test has been a practical test method conventionally used with the ballistic pendulum test and the Trauzl lead block test to establish explosive power. This test is prescribed in JIS K 4810−1979 in Japan. The principle is that the projectile in the bore is propelled out when the sample in the bore explodes and the mortar is swung backward in reaction. The explosive power of the sample is evaluated by the maximum swing length.

The weight of the conventional mortar is about 450kg and the mortar is suspended on a pendulum about 3 meters long. A 10g sample is inserted in the cylindrical container with a diameter of 24 mm made of tin foil. A projectile of about 17 kg is attached and the sample is initiated by a No.6 electric detonator. The explosive power is measured by the swing angle. Some problems exist with this instrument like the projectile being too heavy and the space of the bore being too large for evaluating the explosive properties of unstable substances. The MKIII ballistic mortar was developed by Turner[62] of the Royal Armament Research and Development Establishment (RARDE) in the UK. The same apparatus was installed at the Safety Engineering Laboratory of Tokyo University (Hodogaya−ku Yokohama) in 1983 and at the Hodogaya Factory of Japan Carlit Co.,Ltd in 1986. The weight of this mortar is about 110 kg; is smaller than a conventional one. The sealing in the bore is good, and it is suitable for measuring the explosive properties of unstable substances weaker than explosives.

(2) Structure of the MKIII Ballistic Mortar

The MKIII ballistic mortar introduced in RARDE was used to evaluate many unstable substances, and standardization of procedure and structural revision were carried out.



(a) (b)

Fig. 3.103 Appearance(a) and cross−section(b) of MKIII D ballistic mortar

(a) MKIII D ballistic mortar

The kiner in the tube is made of inducIisa hardand EN2ST greal thata is 357 mm long the bore is 229 mm long with an internal diameter of 25 mm. The open end is 79 mm long and 89 mm in diameter at its widest part; it is formed like a venturi. The mortar is suspended by four stainless steel cables 3mm diameter with a suspension length of 2080 mm. The cables are attached at either end by bottle screws and pivots. The recorder, placed approximately 75mm under the mortar, measures the horizontal component of the swing length with a pen attached to the mortar. The outline and cross section of the MKIII ballistic mortar are shown in Fig.3.103. The procedure far its use is as follows. Ten g of the material to be tested is placed in a paper charge bag and a No.8 electric detonator is inserted into the material. The paper tube is filled with 57g of tamped Ottawa sand 250−500 μ in diameter. The charge is inserted into the bore, fired, and the swing length is measured.

During the above mentioned test procedure, some controversial points were noted, e.g. a large scatter in the swing length was found, safety precautions for detonators were insufficient, and with aluminium foil wrap for the sample excessive explosive powers were obtained, because aluminium reacted as fuel with oxidizing materials. Therefore, some revisions were incorporated.

To obtain reproducible data we used a 15 ml commercial glass vessel and a copper cylinder (150g weight) for safety. To fix the sealing space in the bore we used the paper tube and filled it with 70g of Ottawa sand and a rubber plug.

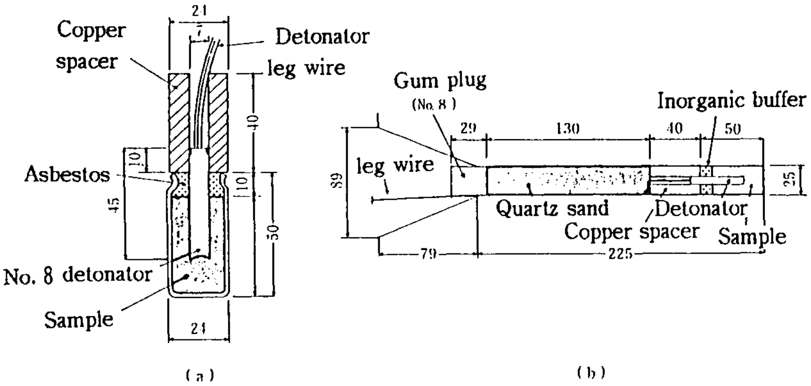


Fig. 3.104 Cross−section of sample vessel(a) and change inside mortar(b)

(b) MKIII E ballistic mortar

The MKIII D ballistic mortar experienced structural damage to its body as shown in Fig.3.105 after about 400 firings. The damage was thought to be caused by the concentration of stress induced by reflections of shock waves. Therefore, we revised the mortar body to make the stress concentrate on the most fragile parts. We divided the liner of the mortar body into 3 parts to replace the liner part damaged by the explosions easily. This nw design is designated MKIII E. The cross section is shown in

Fig.3.106.

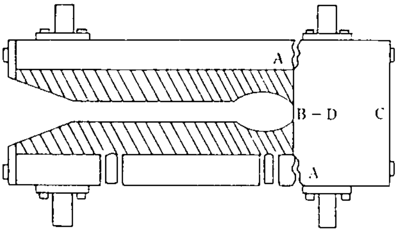


Fig. 3.105 Damage to the MKIII D ballistic mortar

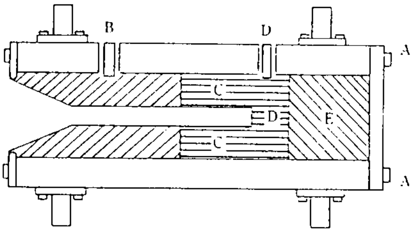


Fig. 3.106 Cross-section of MKIII E ballistic mortar

We used two types of sample vessels, one for an oxidizing material, and the other for a general unstable material. The sample vessels for an oxidizing material is not made of combustible materials and is shown in Fig.3.104(a). For a general unstable material we used a polyethylene lid and inner tube as shown in Fig.3.107. The polyethylene lid and inner tube could also be used safely for a liquid material, because material could not come into contact with the detonator. Moreover, we adopted a test procedure without tamping shown in Fig.3.108 that was found to be sufficiently effective for sensitive materials.

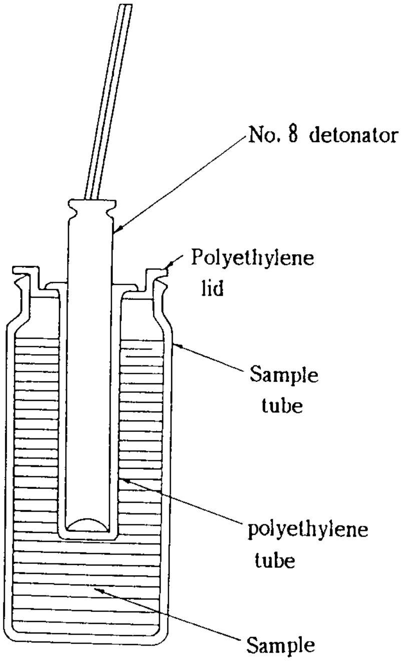


Fig. 3.107 Sample set-up

(c) MKIII F ballistic mortar

After some one hundred firings, bolts A and B, shown in Fig. 3.106, became so tightly fixed to the body that the liner, C, could not be removed. To solve such problems, a clearance between the inner liner and the outer steel tube was provided. Prisdesign is designated MKIII F, and the cross section of this mortar is shown in Fig.3.109. As a result we could clean easily after firing, observe any damage and the mortar became cheaper to operate.

(d) MKIII G ballistic mortar

Many unstable materials were tested and it was found that for some insensitive materials the B' value might be affected by the weight of the projectile. In this case a heavier projectile must be used. A 11.3 kg projectile was inserted into the hole of the mortar. The cross section of this is shown in Fig.3.110. Simultaneously, less sample mass needed to be tested with this projectile so the mortar body was more durable. At present a 2kg projectile is used as the standard.

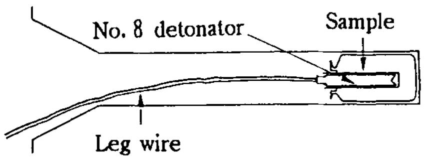


Fig. 3.108 Charge of sample
(no filling material)

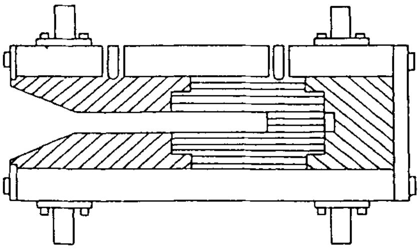


Fig. 3.109 Cross-section of MKIII G ballistic mortar

(3) Properties of the MKIII ballistic mortar test

In RARDE B the value as the relative explosive power verses picric acid is calculated with the following equation.

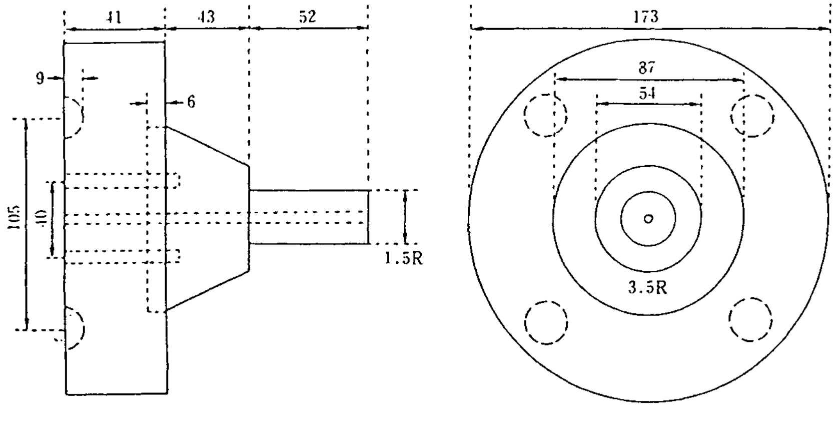


Fig. 3.110 Cross-section of 11.3 kg of the projector

$$B = \frac{d_2^{\,2} - d_0^{\,2}}{d_1^{\,2} - d_0^{\,2}} \times 100$$

where d_0 : the length of the swing with a inert material.

d_1 : the length of the swing with 10g of picric acid.

d_2 : the length of the swing with a test charge.

We examined the variation of the swing length with the charge by using 0-10 g of

TNT. The swing length increased linearly with the weight of the charge as shown in Fig.3.111. Thus, we propose the following B' value as an index instead of a B value.

$$B' = \frac{d - d_0}{d_1 - d_0} \times \frac{10}{W} \times 100$$

where w : the weight of the test charge.

d_1 : length of the swing with 10g of TNT.

d : the length of the swing with w g of the test charge.

We compared the weight of the charge with $d^2 - d_0^2$ or with $d - d_0$ and concluded the following based on Fig. 3.122: for TNT, the B value seemed proportional to the second order of the weight of the charge, while the B' value from the MKIII ballistic mortar test seemed proportional to the first oeder of the weight of th charge. Therefore, the B' value was defined as the explosive power. We found the MKIII ballistic mortar test was excellent in most cases because there was nor relationship between the B' value and the weight of the charge. On the other hand there were some problems in Trauzl's lead block test. First, lower lead block expansion values were obtained for materials with slow detonation velocities i.e. black powder or some organic peroxides. Second, there was not a linear relationship between the lead block expansion value and the weight of the charge even for a powerful explosive. In conventional ballistic mortar tests the ballistic mortar value S did not increase linearly with the weight of the charge (See Fig.3.113.)

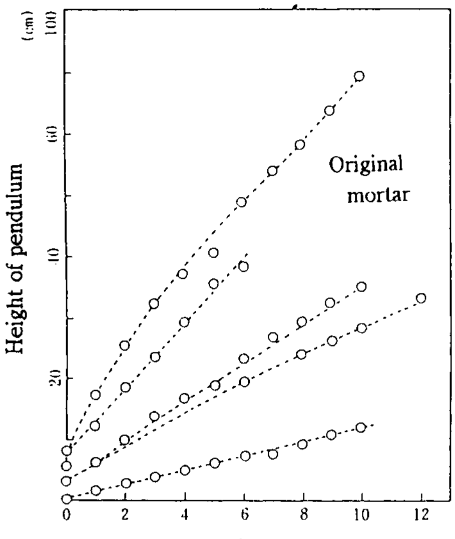


Fig. 3.111 Relation between samples and height of pendulum of MK III ballistic mortar

For recording, a pencil lead protected in a brass tube from the shock of the explosion was used, and it recorded by sliding on the paper. To know about the effects of the swings on the recording pen, we observed the oscillating behaviour of the mortar with and without a pen. The results are shown in Fig.3.114 and Fig.3.115. We could see that the periodic time of the oscillation was 3.24 sec. under both conditions with and without a pen. In the case of the test without pen, it was found that the results obeyed the general reducing oscillation curve, where frictional resistance should be proportional to velocity. The equation was,

$$X(t) = a \cdot \exp(-0.00323t) \cdot \sin(2\pi t/3.24)$$

In the case with a pen, it showed a much different oscillantion curve where the amplitude decreased linearly with time. We could obtain the approximate equation for this case with a pen by adding a correcting term to the equation.

$$X(t) = a \cdot [\exp(-0.00323t) - 0.0079t)] \cdot \sin(2\pi t/3.24)$$

The length of the mortar swing used to calculate the B' values should be obtained from X(t) at a 1/4 periodic time.

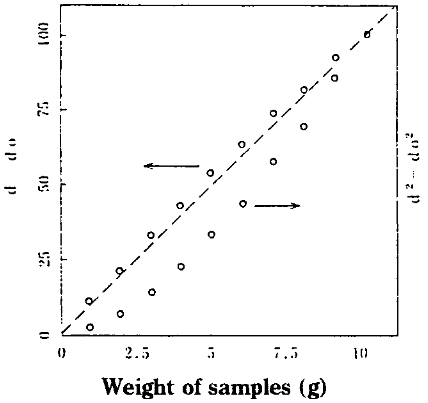


Fig.3.112 Variation of values in the ballistic mortar test with weight of samples (MKIII, sample:TNT, projector:2kg)

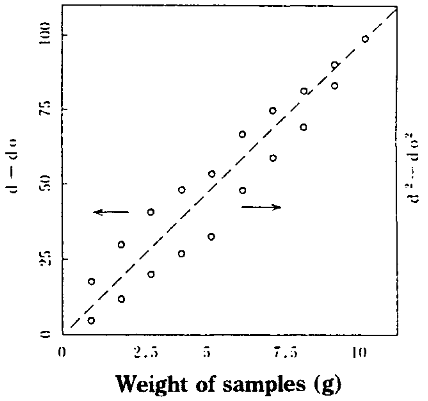


Fig.3.113 Variation of values in the ballistic mortar test with weight of samples (Original, sample:TNT, projector:17.4kg)

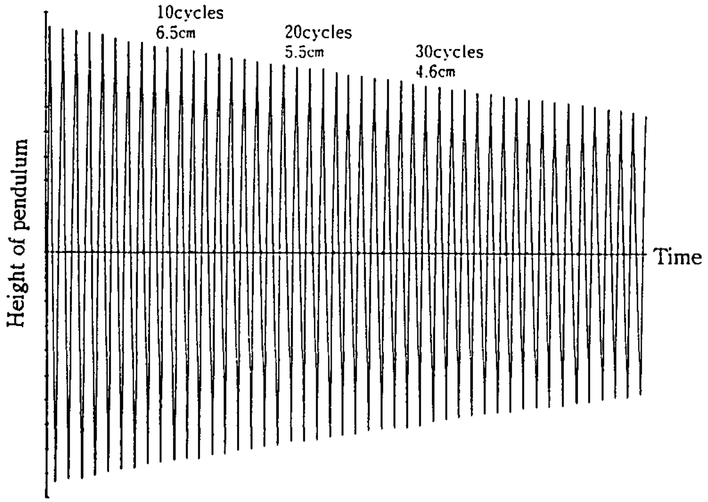


Fig. 3.114 Vibration of ballistic mortar MKIII (without pen)

The relationship in the length of the mortar swing between the device with a pen, d', and without a pen, d may be derived, from equations (1) and (2).

$$d = 1.0064\, d'$$

Hence, the initial velocity of the mortar V, can be calculated by differenciating X(t) and one obtains the following equations for swing d' and d.

$$V = 1.94\ d$$

$$V = 1.93\ d'$$

From the above result, the error derived from the frictional resistance of the pen should be less than 1% and within the limits of experimental variations, and the frictional resistance of the pen should not influence the B' value.

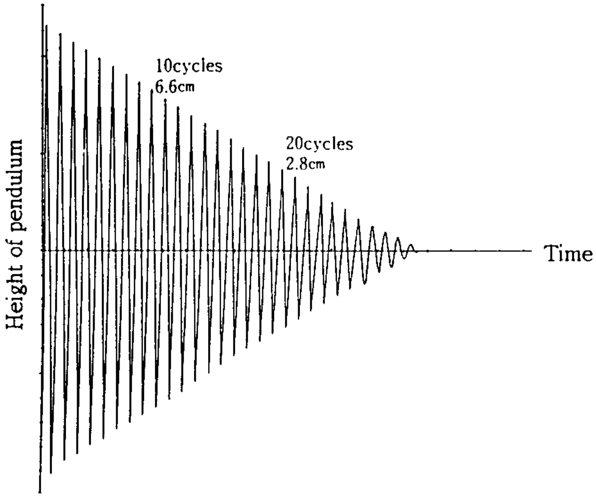


Fig. 3.115 Vibration of ballistic mortar MKIII (with pen)

(4) PETN equivalence

The first fact we need to establish when using the ballistic mortar to measure sensitivity, is the relationship between the weight of the initiator and the swing of the mortar. Fig.3.116 shows this relationship using PETN as the initiator. The plot is linear. Secondly, we examined the relationship between the class of the detonator and the swing of the mortar. With only a detonator, it was found that a No.0 detonator was equal to 0.18 g PETN and a No.6 detonator was equal to 0.6 g PETN. The PETN equivalence of a No.0 detonator was

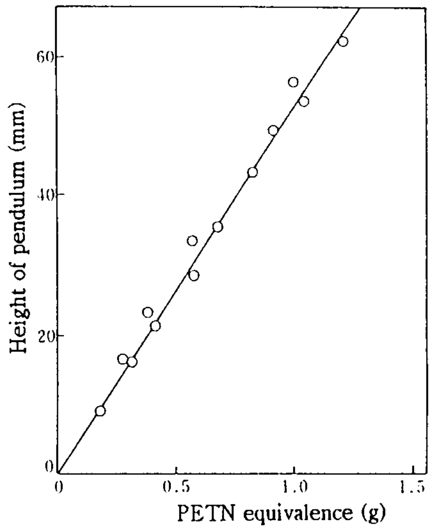


Fig. 3.116 Relation between PETN equivalence and height of pendulum

0.18 g and that of a No.6 detonator was 0.6 g. Therefore, the PETN equivalence with a No.0 detonator plus 0.2 g PETN is 0.38 g.
In the experiment a detonator, PETN and 5g of a test charge were fired and the net swing of the mortar for the test charge was calculated by deducting the swing of the firing with only a detonator and PETN from the measured swing of the mortar with the charge. This value is the PETN equivalence of the test material.

(5) The variable initiator test

An explosive material explodes completely, partially or never explodes in response to the weight of explosive used as the initiator. For example, ANFO did not explode with only a No.6 detonator but exploded completely with a 100 g booster.
This tendency was observed in the experiments using the MKIII ballistic mortar for measuring shock sensitivity. As shown in Fig.3.82, the sample containers were made for using the MKIII ballistic mortar as a shock sensitivity test device. The speial contaires impart greater reproducibility to the experiment and more safety. Fig.3.83 shows the weight of the initiator (PETN equivalence) on the x−coordinate. It is plotted against the net length of the mortar in the y−coordinate, and points are generated from the experiments with ANFO, IREMITE (water gel slurry explosive) and No.3 KIRI dynamite.
The curve from ANFO is S −shaped with 0.6 g of PETN equivalence as the initiator. By firing with 0.6 g of PETN equivalence (No.6 detonator), 10% of an ANFO charge was decomposed explosively. But this explosion did not reach all of the charge. By firing with more than 0.9 g of PETN equivalence, all of the 5g charge of ANFO explodes and, as the net swing of the mortar is longer, the static explosive power is stronger. Within the data shown in Fig.3.83 the explosive power decreases in the following order: No.3 KIRI dynamite > ANFO > Iremite. It is reasonable to assume that No.3 KIRI dynamite is the strongest explosive. But it is strange that the explosive power of ANFO is greater than that of the slurry explosive, because the detonation velocity of slurry explosive is faster than that of ANFO. The total explosion energy of the slurry explosive is almost as large as that of ANFO, but because of the detonation velocity of the slurry explosive is fast, the static explosive power of the slurry explosive is relatively small.
Almost all of a charge of No.3 KIRI dynamite explodes by firing with only a No.0 detonator (PETN equivalence 0.18g). On the other hand Iremite explodes incompletely and ANFO does not explode. The shock sensitivity of dynamite seems to be higher than that of Iremite or ANFO.
By firing with only a No.6 detonator (PETN equivalence 0.6 g), Iremite explodes completely, but ANFO explodes only partially. It seems that ANFO is less sensitive than Iremite.

Neither No. 3 KIRI dynamite, Itemite nor ANFO burns when contacted with a small open flame. Hence, those materials might not burn when partially decomposed in these experiments. The order of the compounds with respect to their relative safety against shock is No. 3 KIRI < Iremite < ANFO. To compare the sensitivities of the materials in Fig. 3.83, one may compare the curves. The further to the right a curve lies, the lower the sensitivity of the compound.

(6) Small gap test

The variable initiator test was useful for assessing shock sensitivity for relatively insensitive explosive materials. This test could not be applied to relatively sensitive explosive materials exploded completely by a No.0 detonator. Therefore, the small gap test was developed. A shock energy less than that from a No.0 detonator was necessary for this test, and this weak a shock was obtained by placing, polyethylene cards between the No.0 detonator and the material. The strength of the shock was varied by changing the number of cards. A typical sample vessel is shown in Fig.3.84.

As more sensitive materials were used in this test, 1g of a charge was used for safety. There are extremely sensitive materials among these explosive materials, and even 1g of a charge may be too dangerous. The small gap test can be applied for relatively sensitive materials, but it must not be used for highly sensitive ones. Such materials should be subjected to the drop ball test.

The data treatment is different for the small gap test the variable initiator test. The explosive materials evaluated in the small gap test are ignited and combusted easily by an open flame. Some materials in the closed space underwent deflagration to detonation. In the small gap test it seems to be dangerous when the exothermal decomposition occurs partially and complete explosion is incomplete. In the small gap test we must assume that a dangerous reaction has occurred when smoke or a flame is seen without explosive reaction.

Benzoyl peroxide (BPO) is used to bleach flour and to produce some plastics. Several incidents have occurred involving BPO. Their cause seems to be the use of BPO without any recognition of the high sensitivity of this material. In the drop hammer test with a 5 kg hammer the height of 50% explosion is 10 cm. Therefore material belongs in the group of highly sensitive materials. On the other hand in the small gap test BPO exploded with 4 mm gap width, but did not explode completely with a 5mm gap. This shock sensitivity is half-way between picric acid and tetryl. After the experiments with more than a 5 mm gap width, smoke produced by decomposition products of BPO exited the bore of the mortar; even when using 40 mm of gap width, smoke came out. These characteristics show the possibility that dangerous reactions occur and that the shock sensitivity of BPO is very high.

Dynamite behaves strangely in the small gap test. Fig.3.117 shows the results of dynamite and carlit. Carlit has the same tendency as a high explosive like PETN. As the shock weakens, carlit explodes completely without decreasing explosive power till a point where it does not explode entirely. On the other hand in the small gap test No.3 Kiri dynamite has half the explosive power determined by the variable initiator test. The rate of explosion of No.2 Enoki dynamite becomes smaller as the shock weakens near the non−detonation point. The reason for this is unknown. This tendency for dynamite was found only experimentally. When dynamite is misfired and remains, it can be exploded by the bit of a rock drill. Such a possibility with slurry explosives or ANFO seems to be small. One reason is that the sensitivities of dynamites were lower than those of the slurry explosives or ANFO. But one must be careful, even if insensitive slurry explosives or ANFO with detonators are misfired and remain, because impact accidents between drill bits and the explosives might still occur.

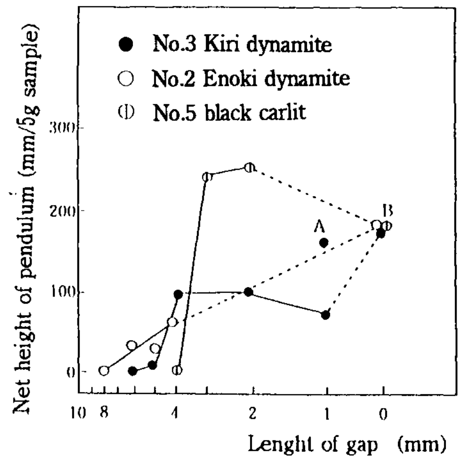


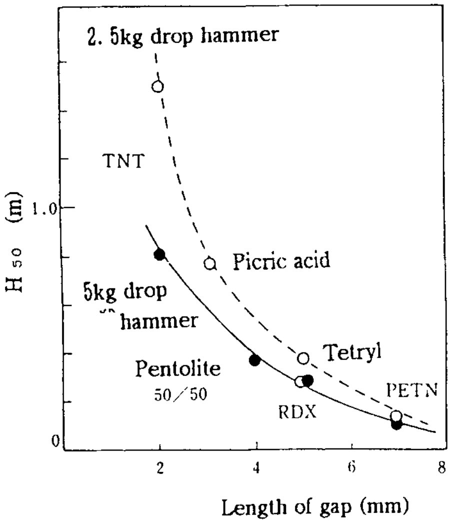
Fig. 3.117 Test results of small scale gap test of Dynamites and black carlit

(7) Comparing the results of the small gap test and other sensitivity tests

The data from conventional sensitivity tests for explosive materials and the sensitivities determined in the small gap test are shown in Fig. 3.118 – 3.120. The drop hammer test was the most popular test. The results are from the 50% explosion test carried out in USA. Fig.3.118 compares the experimental results with a 2.5 kg or 5 kg hammer in the type 12 drop hammer test machine at Los Alamos National Laboratory in the USA and the results from the small gap test. A good correlation between these data 0 is obtained. Fig.3.119 compares the results in the small gap test and the results in the conventional test carried out at two laboratories in the USA. The open circles are data from the NSWC (National Surface Weapon Center), and the filled circles are data from the LANL (Los Alamos National Laboratory).

The priming sensitivity of the explosive materials depends on the physical condition of the materials. Data from powdery materials is shown.

Though a scatter in the data from pentolite (PETN/TNT = 50/50) is shown, a good correlation between the small gap test and the conventional gap test is observed. This may occur because both tests are based on the same. Fig.3.120 shows a comparison between the results of the small gap test and the BAM friction test. The results in the BAM friction test cover the class of materials with dangerous properties. Class 1 shows contains the most sensitive materials and Class 7 in contains the least sensitive materials; the latter not can be measured in the BAM friction test.



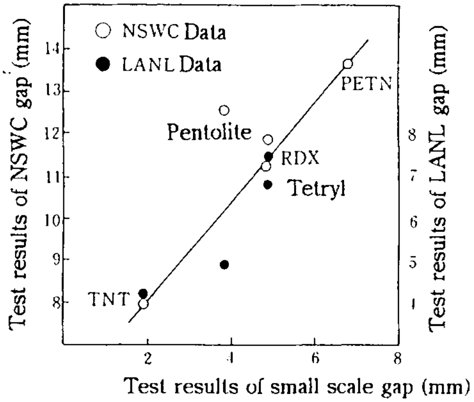


Fig. 3.118 Test results from small scale gap and drop hammer sensitivity tests

Fig. 3.119 Test results from small scale gap and US gap tests

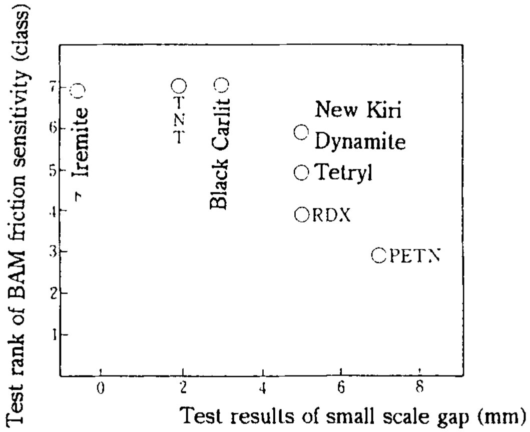


Fig. 3.120 Test results from small scale gap and BAM friction sensitivity tests

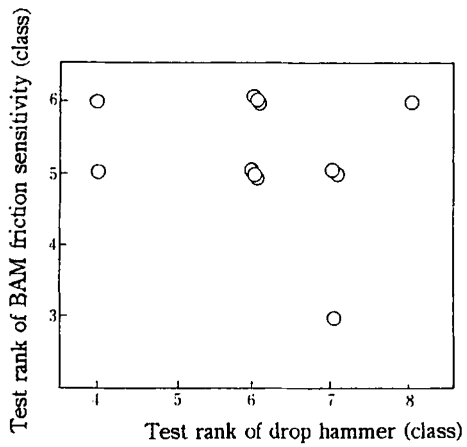


Fig. 3.121 Test results of mixtures of KClO4 – Al in the drop hammer sensitivity and friction sensitivity tests

The materials requiring less than 3 mm of critical gap width in the small gap test cannot be measured in a BAM friction test. More sensitive materials can be measured in both tests and show a reasonable correlation. But the correlation between the results of the drop hammer test and the friction test is not always good for the mixtures of oxidizer and fuel. Examples of this are shown in Fig.3.121. In these examples the samples demonstrate high blow sensitivities but low friction sensitivities or low blow sensitivities but high friction sensitivities. The interpretation of the results seems to indicate four possibilities.

(a) These results are correct.

(b) Both experiments with the mixtures result in data with considerable seatter.

(c) The accuracy is not good in the drop hammer test for mixtures.

(d) The accuracy is not good in the friction test for mixtures.

Regretfully, only two small gap tests of these mixtures were carried out. The results of ammonium perchlorate – aluminiun powder – sulfur and potassium perchlorate – aluminium powder – titanium powder, are shown in Fig.3.97. The mixture of potassium perchlorate–aluminium powder is found to be highly sensitive. Considering the results of small gap test it seems reasonable that the class identified by the drop hammer test or the friction test should be 2 – 3 grade.

3.7.6 The variable intiation test using the underwater explosion

01 Name of the method

The variable intiation test using the underwater explosion.

02 Propenty evaluated

Shock sensitivity of materials with relatively low sensitivity.

03 Equipment and materials

An explosion resistance pool must be more than 3m in diameter and 2m deep. Samples are exploded at a depth of 1 m in the center of the pool.

An iron frame or a bridge supports samples and a pressure sensor is prepared. To detect the first pulsation of bubbles by an explosion, a pressure sensor or a microphone and a digital recoder and a data recorder are induded.

Sample bottles are the same as in the variable initiation test using the ballistic motar. No.0, No.1, No.2, No.3 and No.6 electric detonators are prepared. PETN powder is used to increase initiation charge.

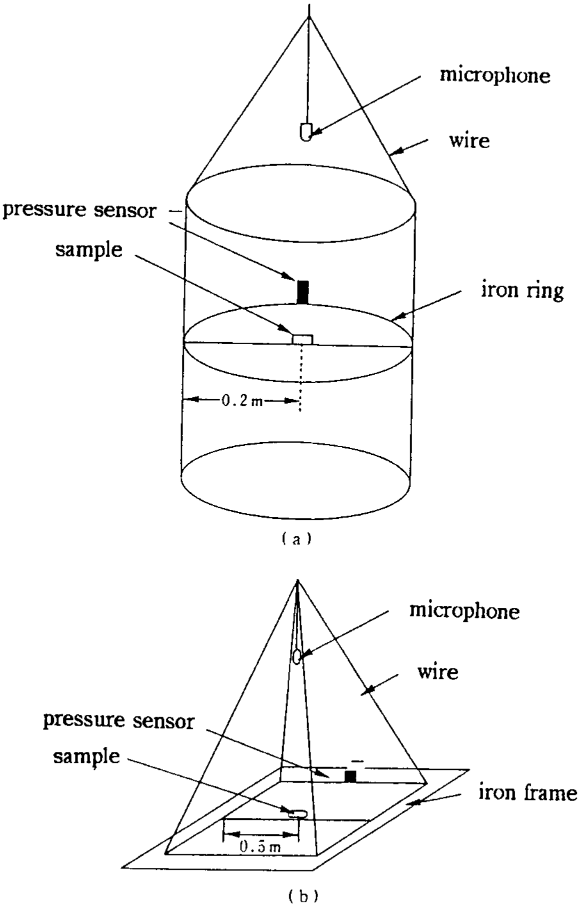


Fig. 3.122 Supporting frames for the underwater explosion test

The equipment used by the authors is as follows.
Using two kinds of supporting frame shown in Fig.3.122, the sample was fixed in the center of the frame, sunk to a specific depth by a crane and initiated. The frame shown in Fig.3.122(a) was used to determine the bubble energy of initiators at a depth of 0.4 m. In the variable initiation test and the variable sample test, in which larger charges were studied, the set-up shown in fig. 3.122(b) was used for a depth of 1.0 m. Thin wire was used to bind the components in place. The atmospheric pressure needed i the calculation was measured at the site every hour.

O4 Test proceduer

O4.1 The test of initiators and inertia materials

Variable amounts of PETN in 0.1 g increments are charge into inner tubes. The tube is plugged with a 15 mL sample bottle containing inert material. A No. 0 or No. 6 electric cap is fixed on the bottle and detonated under water. The first pulsation period is measured.

O4.2 The variable sample test

This test is not done on materials judged gighly sensitive by the drop ball test or the small gap test. On-half gram of sample is loaded into a 10 or 15 mL sample botte The 10 mL bottle is chosen for samples of high density to avoid empty space in the bottle. A polyethylene plug with a hole is put on the sample bottle.

From 0.1 to 0.6 g of a PETN charge is loaded into an inner tube. A maximum charge of 0.3 g is loaded when a No. 1 cap is used.

Fig.3.122 shows a test sample attached to the frame. Leg wires are connected to leading wires, and the connection is sealed to be water-tight. The sample bottle is sunk to a depth of 1 m and is detonated. The first pulsating bubble is recorded.

O5 Evaluation of results

From the first pulsation period(T_b), the bubble energy of the explosion is calculated by the following formula.

$$E_b = 6.84 \times 10^7 P_0^{5/2} T_b^3$$

The values are,

E_b : bubble energy

P_0 : static water pressure

T_b : the first pulsation period

The net bubble energy (Net$-E_b$) is the difference between the sample and the inert material(talc) plus initiator. The PETN equivalent in grams is defined at the weight of PETN which produces the same bubble energy as inert material plus initiator. Table 3.39 shows (Net $-$ E_b) and PETN equivalents of initiators measured by Kaneko et al. (Net $-E_b$) is proportional to the initiating ability of the initiators.

Net bubble energy curves are generated by ploting (Net − E_b) vs. the bubble energy of initiators.
Fig.3.123 shows an example.

O.6 Interpretation
Sensitivity is judged by the shape of net energy curves.

Table 3.39 Net bubble energy ($\triangle E_b$) and PETN equivalency of initiators

Initiator	$\triangle E_b$(kJ)	PETN equivalent (g)
No.0*	0.20	0.18
No.1*	0.32	
No.0+0.1gPETN	0.39	0.28
No.2	0.44	
No.3	0.56	
No.0+0.2gPETN	0.58	0.38
No.0+0.3gPETN	0.74	0.48
No.6	0.68	0.60
No.6+0.1gPETN	0.88	0.70
No.6+0.2gPETN	1.06	0.80
No.6+0.3gPETN	1.24	0.90
No.6+0.4gPETN	1.42	1.00
No.6+0.5gPETN	1.60	1.10
No.6+0.6gPETN	1.78	1.20

* electric detonators.

3.7.7 The small gap test using underwater explosion

P.1 Name of the method
The small gap test using an underwater explosion.

P.2 Property evaluated
The shock sesitivity of highly sensitive explosive materials.

P.3 Equipment and materials
A pool 3 m in diameter and 2 m deep is neccesary for the test. Fig.3.125 shows the apparatus. Measuring instruments are the same as in the variable initiation test. Sample bottles and inner tubes are also the same as those used in the variable initiation test.

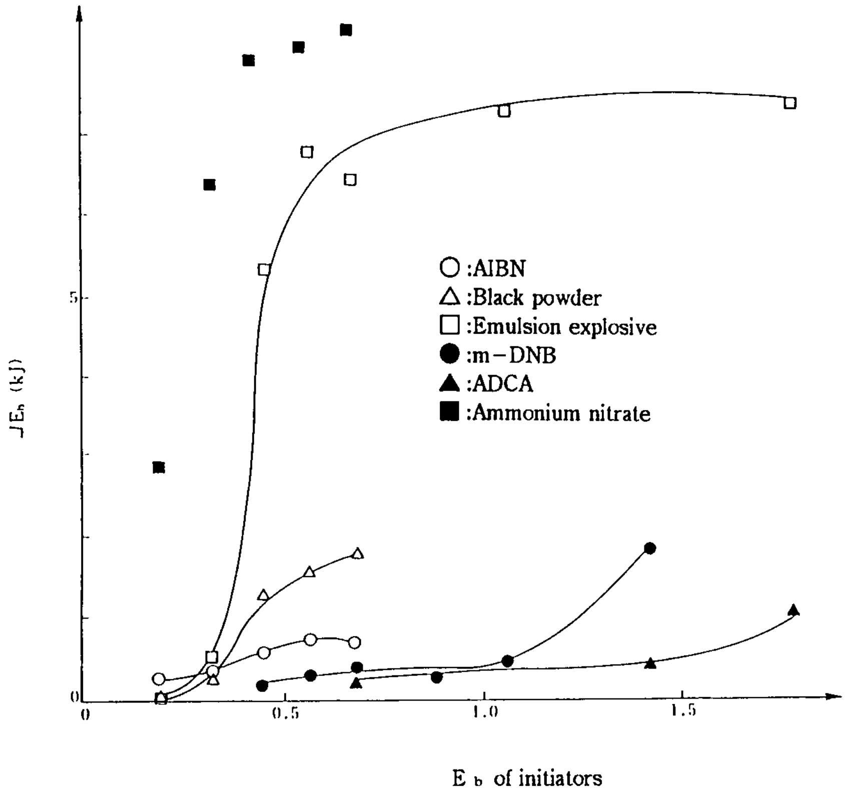


Fig. 3.123 Plot of Net – Eb of explosive materials and unstable materiala vs. Eb of initiators

P.4 Test procedure

P.4.1 Measuring the first pulsation period of No.0 cap within an inner tube

A No.0 cap inserted into a plastic inner tube is sunk to a depth of 1 m deep and detonated. The first pulsation period of the bubble is measured by a pressure sensor placed 1 m away from the sample.

P.4.2 Measuring the first pulsation period of the explosion

Twotently g of sample is charged into a plastic inner tube, and some polyethylene cards, 1.0 or 2.0mm thick, are put on it. A No.0 cap is placed on them. The top of the sample is sealed with waterproof tape. This sample assembly is submerged to a degetle of 1 m and detonated. The first pulsation period of the bubble is recorded.

P.5 Evaluation of results

The calculation of bubble energies (E b) is done the same way as in the variable initiation test. Curves describing the strength of the explosions are prepared by plotting

Eb vs. gap length. Fig. 3.126 shows examples of these curves. Shock wave energy is an alternative variable to Eb.

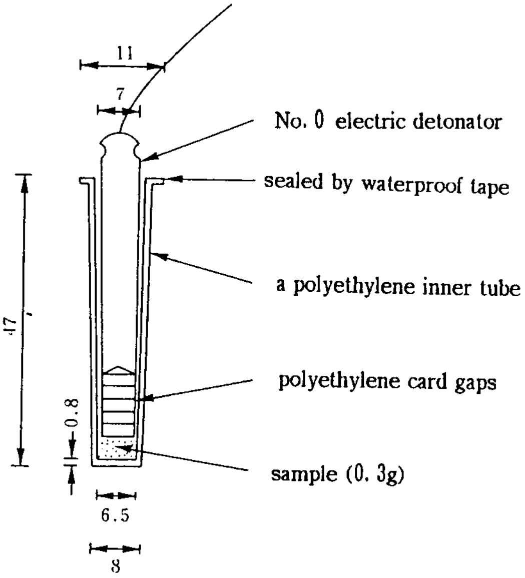


Fig. 3.124 A test assembly for the small gap test

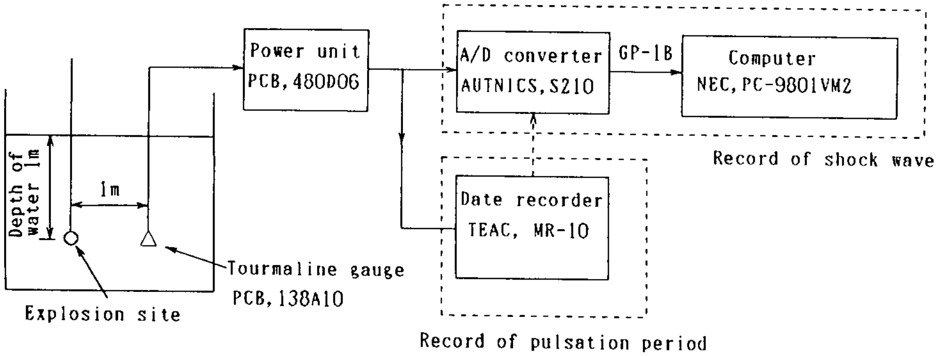


Fig. 3.125 Apparatus for measuring underwater explosion

P.6 Evaluation of the results

Sensitibity is assessed by comparing the shape of the curves.

P.7 Application of small gap test and the variable initiation test

Fig.3.127 shows an example of a comparison of the data from the small gap test and the variable initiation test using an underwater explosion.

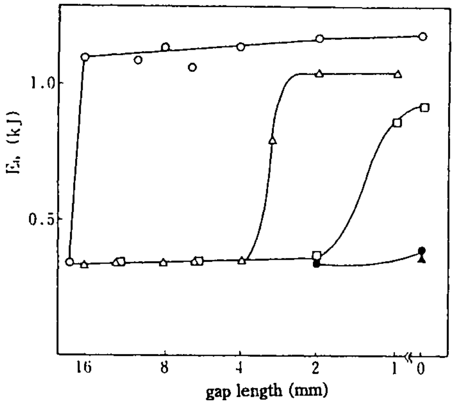


Fig. 3.126 Plot of Eb vs. logarithm of gap length
○ :100%PETN △ :90%PETN □ :80%PETN
● :70%PETN ▲ :60%PETN diluent: water

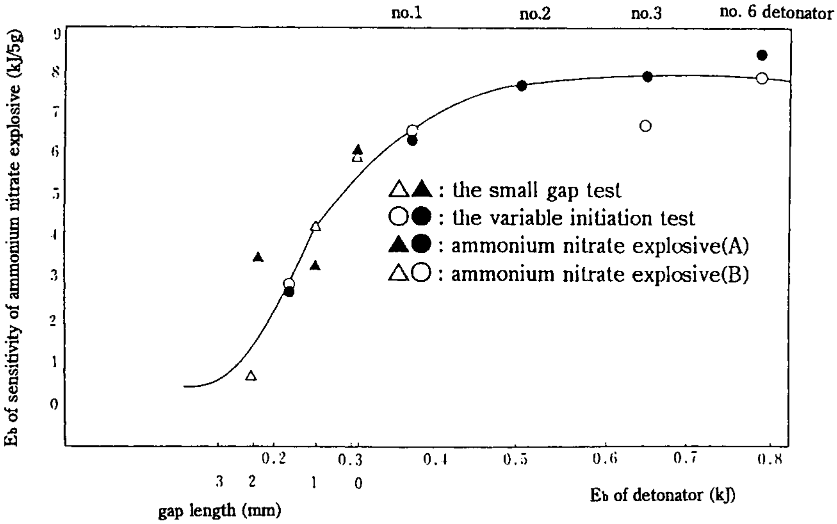


Fig. 3.127 Shock sensitivity of ammonium nitrate explosive

3.8 Detonation–Propagating Tests: Tests for the Possibility of Explosion

3.8.1 Introduction

For self–reactive substances typical dangerous reactions are detonation, deflagration and thermal explosion. The possibility of detonation and the propagation of violent deflagration is the most important property to determine regarding the hazards of self−reactive substances.

The BAM 50/60 steel tube test, the TNO 50/70 steel tube test, and the gap test of the America Bureau of Mines are well−known [5] .These methods are useful to assess detonation−propagation and are described in the earlier book [1] .

However, these methods are not able to assess the deflagration−propagation of less−sensitive materials because it is difficult to determine if deflagration−propagation occurs if fragmentation of the steel tube or no deformation on the verification plate in these methods takes place.

The variable initiator test using the MKIII ballistic mortar and the ballistic pendulum is very effective to evaluate these materials [55, 68] . The probability of occurance of deflagration can be determined from the strength of explosion in the ballistic mortar or ballistic pendulum test. However, this method cannot be used for detonating materials that may damage the test equipment.

The authors discussed in the following such detonation−propagation tests as the 50/60 steel tube test under sand, the 50/60 steel tube test under water and the variable initiator test using the ballistic mortar or ballistic pendulum. If one or more of these tests is used, the detonation−propagation of self−reactive substances can be evaluated. The limitations of these methods is listed in Table 3.40.

Table 3.40 Useful detonation−propagating tests

Substances	test methods
detonation materials	50/60 steel tube test under sand 50/60 steel tube test under water
deflagration materials	50/60 steel tube test under water Variable initiator test using MkIII ballistic mortar Variable initiator test using ballistic pendulum

3.8.2 50/60 steel tube test under sand (Q) [51, 69]

Q1 The name of test method

50/60 steel tube test under sand

Q2 Property evaluated

The probability of self−sustaining detonation and no detonation

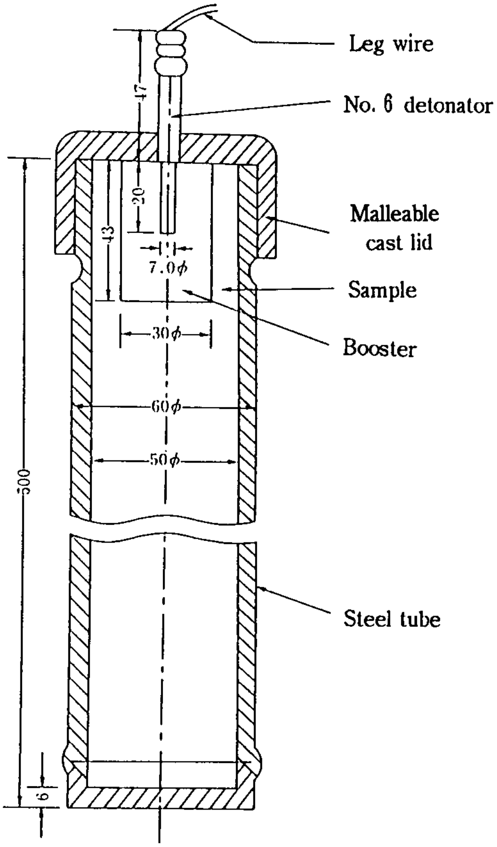


Fig. 3.128 Sample set–up for the 50/60 steel tube test

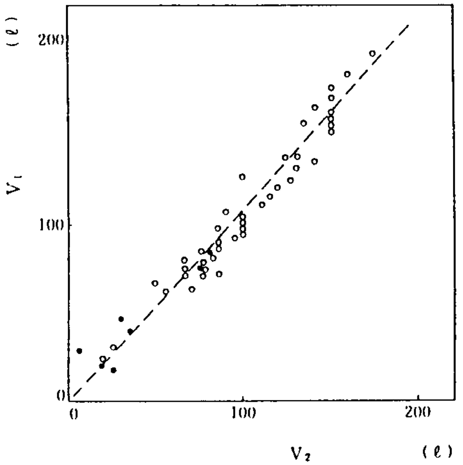


Fig. 3.129 V2 vs. V1

Q3 Installation and materials

Q3.1 Test site

To provent fragments from escaping the test site, the field must be an explosion test field 1 m in deep and 3m × 3m in size.

Q3.2 Steel tube

A cold-drawn seamless steel tube 5mm thick with an inner diameter of 50mm and a length of 500mm is used. The bottom end is made from steel plate 6mm thick by melting method. The cover is made from malleable cast iron and with a screw in its center. On the cover is a hole with a diameter of 7.5 mm so that a No. 6 detonator (JIS K 4807) can be inserted into the tube. The volume of the tube is about 1 liter.

Q3.3 Booster

The booster is formed from RDX(95%) and wax(5%) by compression with 1500kg/cm ^{2} of pressure. The diameter of the booster is 30mm, and its length is 43mm. On the upper end a hole 7mm in diameter and 20mm deep is formed to insert a detonator.

Q3.4 Polyethylene tube

To provent the unstable tested materials from contacting with the steel tube, the sample is first put into a thin polyethylene tube 50mm diameter, then into the steel tube.

Q4 Test procedure

A powdered sample is put into a polyethylene tube, then into the steel tube. A booster is placed on the upper surface of the sample, and the mass of sample is recorded. A wooder rod 6.8mm in diameter is inserted into the hole on the booster to enable the insertion a detonator, and the cover is tighted by hand. A detonator is inserted into the hole of the booster from the hole in the cover, and the tube is placed horizontally in the sand at a depth of 60cm.

Leg wires from of the detonator are linked with the initiation wire, then connected to the initiator. After verifing that there is no one in the dangerous region of the test site, the sample is ignited.

The long diameter(a), short diameter(b) and depth (h) of the crater formed are measured, and the volume of the crater is calculated according to the following formula:

$$v = \pi abh/12$$

The steel tube or fragments of the steel tube are taken into consideration.

Q5 Evaluation of the results

If detonation is propagated, the steel tube will be totally fragmented and destroyed. In the case of deflagration, most are not completely cracked even though propagation has occured. If the detonation stops, the steel tube will not be totally fragmented. In addition, when detonation takes place, a large crater will be formed in the sand. When detonation does not occur, the crater will be small. The occurrence of detonation can be judged from the size of the crater, but the precision is not as good as when the fragmenting of the tube is used.

Q6 Determination of the result

Detonation–propagation: the whole steel tube is fragmented and destroyed

No detonation–propagation: no cracks in the tube

3.8.3 50/60 steel tube test according to Fire Services Law(Q') The classification test for Class 1 dangerous oxidizing solids

(1) The purpose of the test

The purpose of the test is to determine the detonation or deflagration hazards of solid materials with combustible materials. A mixture of the test sample and a combustible material is put into the steel tube and ignited. The extent of cracking of the steel tube is observed.

(2) Combustible materials

Cellulose powder of particles with a diameter of less than 53 μ m(about 280 mesh) is used as the combustible material. The powder must be stored more than 24 hours in a desiccator containing silica gel under a constant temperature.

(3) Test samples

Generally commercial products are used as test samples. If a product is composed of rod–shaped particle, it can not be put into a steel tube it must be divided into smaller pieces.

(4) Test site

A safe site has explosion laboratories with a sand crater in which the steel tube can be embeded.

(5) Test method

a. A polyethylene tube 50mm in diameter is put into a cold–draw seamless steel tube, the end of which is either fused or screwed into place.

b. A sample consists of the material to be tesed and a combustible agent in a ratio of 3–to–1 by weight in the polyethylene tube. A booster is placed in the center of the sample.

c. The steel tube is closed by a screw–cap with a hole in it.

d. No. 6 detonator is inserted into the booster.

e. The steel tube is embeded in sand and ignited.

f. The extent of cracking of the steel tube is observed.

(6) Evaluation

If the sample detonates, the tested material is hazardous.

3.8.4 Performance of the explosion test under sand (69)

(1) Value of the explosion test under sand

From the measurement of the volume of the crater formed

a. Explosion noise and vibration are weak.

b. The probability of explosion can be determined semi–quantitatively.

c. The test mass can be changed, and it is possible to carry out the test on a large sample of material.

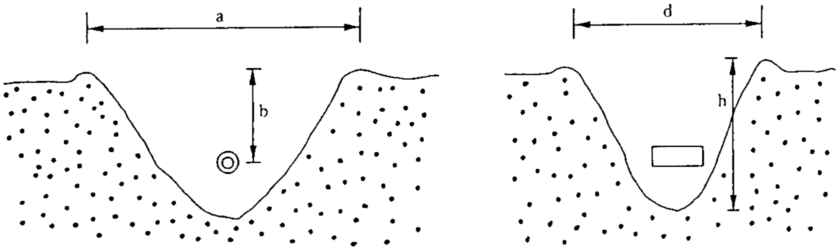
(2) Measuring the volume the crater formed

Two methods may be applied to obtain the volume of the crater. One uses the formula

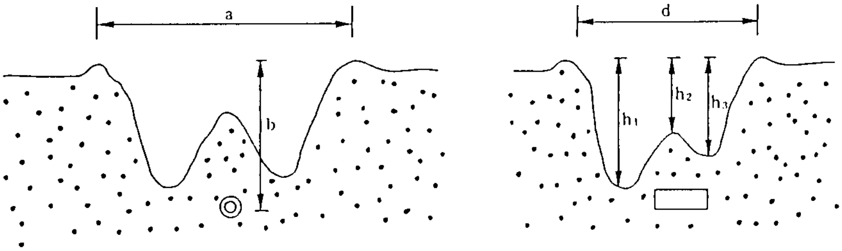
$$V_1 = \pi abh/12$$

in where a, b and h are long diameter, short diameter and depth of the crater respectively. If the crater is irregular in shape as shown in Fig. 3.130(b), the depth h is taken as the average value of h_1, h_2 and h_3. The second method is to measure the volume of sand required to refill the crater. A good correlation between the volumes defined by the methods is illustrated in Fig.3.129.

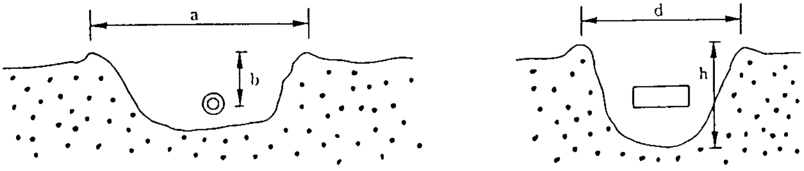
The correlation coefficient is 0.984.



(a) Cone–shaped crater



(b) Irregular crater



(c) Irregular crater resulting from excess charge

Fig. 3.130 Three types of craters from explosions in sand

The value of V_1 derived from a, b and h is generally larger than V_2 , the measure of the sand used to refill the crater. This may arise from the change in the height of sand around the crater after the explosion. The difference between the two methods is not great and the simple measurement suffice. However if the use of extra charge or insufficient charge results in a non−ellipti crater, the value of the volume derived from the measurements of a, b and h may not be correct. Also if the sand under the steel tube is too hard, the conical crater cannot be formed. If the sand becomes hard, the correct volume of the crater will not be obtained. It is recommended same that sand in the same condition always be used.

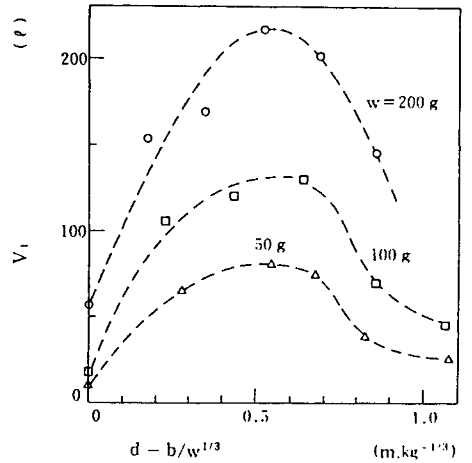


Fig. 3.131 Volumes of craters vs conversion depth of craters produced by explosions in sand

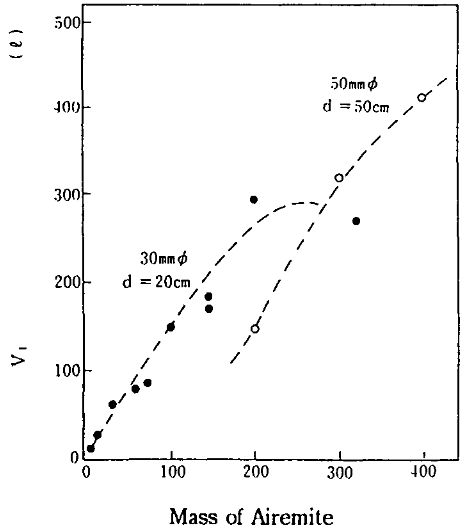


Fig. 3.132 Volumes of craters vs mass of explosive

(3) The depth of the explosive, the mass of the explosive and the volume of the crater

The relationship among equivalent depth (d/W $^{1/3}$) of explosive under the sand, the weight of the explosive (W) and the volume of the crater formed is shown in Fig.3.131. The location of the explosive and the representive shapes of craters are illustrated in Fig.3.130.

The data in Fig.3.131 show that the volume of the crater is greatest when the equivalent depth is about 0.5m. If 100 g of Airemite is used, a regular cone crater can be formed if the explosive is planted at a depth of 10 ~ 30 cm; if 50 g, at a depth is 10 ~ 20 cm, and if 200 g, at a depth is 20 ~ 40 cm. For the 50/60 steel tube test, a depth of 60 cm is reasonable.

When the explosive mass increases, the depth will become deeper than fitting charge. This is because that the deeper of explosive, the weaker of explosion noise, and the effect of closed extent. From these observations the following standard depths are suggested:

for 50 ~ 100 g of explosive, 20 cm,
for 100 ~ 200 g of explosive, 30 cm,

for 200 ~ 500 g of explosive, 50 cm and for 500 ~ 1000g of explosive, 60 cm.

(4) Effect of mass of explosive

Fig. 3.132 shows the relationship between the volume of the crater and the mass of the explosive. Diameters of the explosive charge are 30 mm and 50 mm, their length is 20 cm, and the tubes are composed of vinyl polychloride. There is correlation between the mass of the explosive and the volume of the crater formed. The relationship can be used to determine of detonation-propagation occurs.

(5) Detonation-propagation of ANFO, DPT and DNB

In the shock sensitivity test using the MKIII ballistic mortar, ANFO, DPT and DNB are identified as low-sensitivity explosives of almost equivalent sensitivity[27]. The sample were put into VP-30 and VP-50 tubes and ignited by 50g of Airemite and 100 g of Airemite respectively. The relationship between the length of the explosive charge and the volume of craters is shown in Fig.3.133.

ANFO, DPT and DNB show detonation-propagation in 50 mm VP tubes, and non detonation - propagation in 30 mm VP tubes. The result shows that the three explosives possess almost the same shock sensitivity and the same detonation-propagation tendencies.

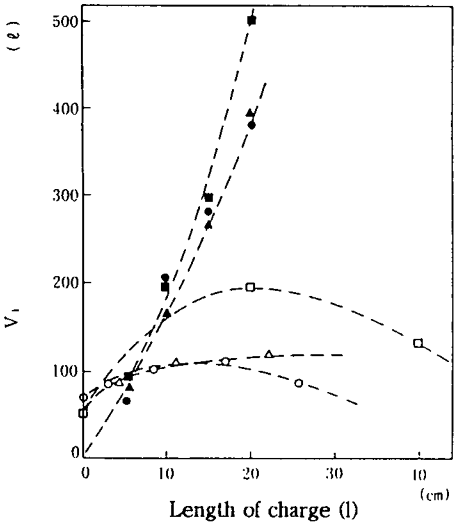


Fig. 3.133 Crater volume vs length of charge for ANFO, DPT and DNB from the explosion test in sand

▲ : ANFO, ● : DPT, ■ : DNB
; 50mm φ, d=50cm
○ : ANFO, △ : DPT
; 30mm φ, d=20cm

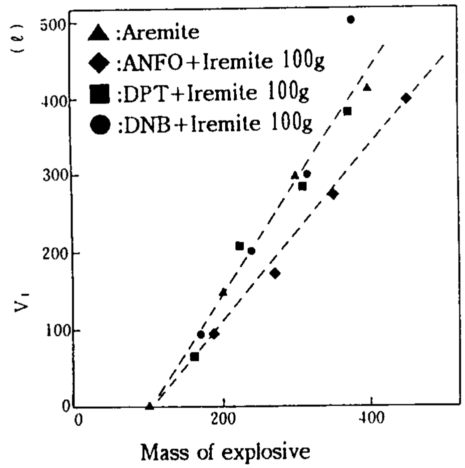


Fig. 3.134 Crater volume vs mass of explosive from the explosion test in sand
PVC tube with d=50cm, inner dia. 50mm

(6) The type of explosives and the volume of the crater

The dependence of the volume of the crater on explosive is shown in Fig.3.134. For the same mass, volumes of craters generated by Areimite, DPT and DNB are almost the same, while that by ANFO is smaller. The explosion powers determined by the MKIII ballistic mortar test are 100%, 60%, 90% and 115% of that of TNT respectively. The trend in the results from the MKIII ballistic mortar test is not consistent with that from the volume of craters. The reason for this difference is yet not clear, and more data are needed.

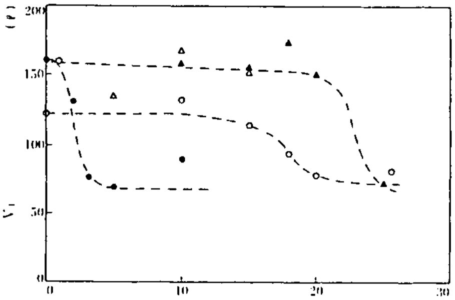
(7) Effect of buffer materials in the gap sensitivity in VPC tubes under sand

For the gap sensitivity test of explosives, the effect of buffer materials was evaluated by using the explosion test under sand. The results are shown in Fig.3.135 and 3.136.

Over the range of the test, sand is the best buffer material, but bubbling styrol and glass microspere are not as effective as air.

However, the good buffer effects of glass microsphere were shown before in the evaluations of shock initiation sensitivity of paper caps[65]. The difference between the two tests arises because the acceptor in this study was Airemite (water gel explosive) with low-sensitivity, while in the previous study superhigh-sensitivity paper caps were used. The two results indicate that buffering effect of glass microsphere is small for a strong impulse but great for a weak impulse, and that the buffering effect of sand is good for either strong impulse or weak impulse.

Iron and polyethylene do not exhibit buffering effects for weak samples[65],



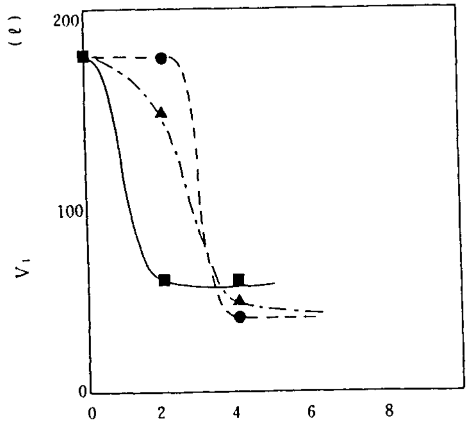
Length of gap (cm)

Fig. 3. 135 Crater volume vs length of gap from Iremite(water gel) explosion in sand

Gap materials: ○ :Air ▲ :Glass microspheres

● :River sand △ :Bubbling styrol

PVC tube with inner diameter of 30mm



Length of gap (cm)

Fig. 3. 136 Crater volume vs length of gap from Iremite explosion in sand

Gap meterials: □ : Steel roller ● : light concrete roller ▲ : Polyethylene roller

PVC tube with inner diameter of 30mm

but do buffer strong impulses. For impulses of certain strength which can ignite Airemite, the order of the buffering effects of tested materials is as follows:
sand > iron > polyethylene > light concrete > air > bubbling styrol ≑ glass microspheres.

(8) Noise of the explosions under sand [70-73]

Data on the noise of the explosions under sand were not recorded in these tests, but Fig.3.137 shows the effect of sand in controlling the noise from explosions when 20g of the explosive is completely covered (measured at 15 and 30 m from the site) and also when 100g of explosive is covered by a dome of sand with one end left open (measured at 30 m). Thirty cm of sand covering 100g of explosive as an open dome reduces the noise level 30 m from the explosion site to 80dB(A).

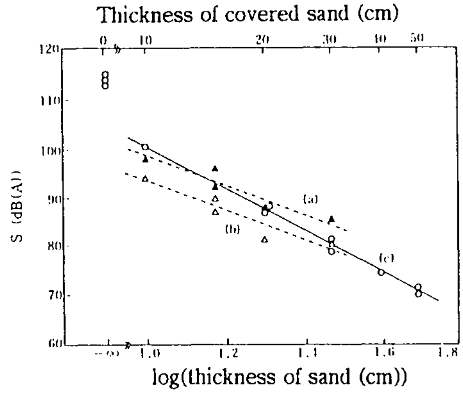


Fig. 3.137 Effect of sand in controlling the noise from explosions
(a)Explosive 20g, on flat ground, from 15m
(b)Explosive 20g, on flat ground, from 30m
(c)Explosive 100g, semi-closed, from 30m

(9) Applications of the explosion test under sand

The explosion test can be used to determine the detonation-propagation of automatic safe flares [69], signal flares [69], airbags [74] ,composite propellants containing HMX [60] and other devices. It is also useful in the development of safe storage for small quantities of explosives [75] based on the capcell method. The method of covering the explosives can also be used to decrease the noise associated with demolition [70-73, 76, 77] . This will further described in Chapter 5.

3.8.5 50/60 Steel tube test under water(R) [102]

R1 Test name

50/60 steel tube test underwater

R2 Hazard evaluated

Propagating detonation and deflagration no self-propagating detonation and deflagration

R3 Installation and materials

R3.1 Test installation

The test apparatus consists of an explosion-proof water tank 10 m in diameter and 5m deep and a bridge and frame to support the sample and a pressure sensor.

R3.2 Steel tube, booster and polyethylene tube

The devices is similar to that used in the 50/60 steel tube test under sand. It is necessary in this test, however, to take measures to water-proof the tube by using adhesive tape .

R3.3 Measurement

It is same as the variable initiator test using an underwater explosion, but the distance of the sensor from the explosion source is 2 m.

Table 3.41 The results of examples of 50/60 steel tube test underwater

Samples	Length of sample(cm)	Sample mass (W) (g)	E_b (kJ)	E_b/W (kJ/g)	Assessment
AIBN 100%	25	261	71.4	0.27	No
AIBN 100%	50	515	59.4	0.12	No
BPO 80%(H_2O)	25	250	73.2	0.29	No
BPO 80%(H_2O)	50	518	62.8	0.12	No
DBPIP 70%(Al_2O_3)	25	250	67.9	0.27	No
DBPIP 70%(Al_2O_3)	50	515	61.9	0.12	No
DBPIP 80%(H_2O)	25	284	62.0	0.22	No
DBPIP 80%(H_2O)	50	590	20.7	0.04	No
DBNPIP 80(Al_2O_3)	50	592	166.6	0.28	Yes
PETN 50%(H_2O)	25	240	228.9	0.95	Yes
RDX 50%(H_2O)	25	300	615.3	2.05	Yes
TNT 50%(H_2O)	25	200	-28.7	-0.14	No
TNT 60%(H_2O)	25	240	-5.9	-0.02	No
Gun powder(coarse)	25	450	228.9	0.51	No-Deto*
Gun powder(coarse)	50	876	311.1	0.36	No-Deto*
Gun powder(powdery)	25	350	59.5	0.17	No-Deto*
Gun powder(powdery)	50	606	6.8	0.01	No-Deto*
NaCl	50	1170	76.3**	1.61**	

* deflagration-propagation, ** data from the booster alone.

R4 The test

A sample is put into a polyethylene tube which is placed into a steel tube, leaving a space for the booster. The tube is sealed with adhesive tape and the mass of the sample is recorded. A booster is placed on the sample, a wood rod with 6.8mm in diameter is inserted into the hole on the booster to enable the insertion of a detonator, and the screw cover is tighted by hand.

The steel tube is hung horizontally 1 m under the steel frame. A detonator is inserted into the hole in the booster through the hole in the cover and the gap between the detonator and hole is sealed with adhesive tape. The leg wires of the detonator are linked with the initiator wire and the connection is sealed with adhesive tape. The steel tube is placed 2 m away from the prassure sensor.

When the measurement system is reading, the initiator wire is connected of the initiator. A signal is sent, then is after which ignition occurs. The first impulsation of the explosion bubble is recorded.

R5 Assessment of results

The method of computing bubble energy (E_b) is similar to that of variable initiator.

$\triangle E_b = (E_b)_{sample} - (E_b)_{salt}$

The value of $\triangle E_b$ determines if an explosion has occurred.

R6 Assessment criteria

Detonation−propagation: the steel tube is completely cracked fragmented.

Deflagration−propagation: the steel tube is incompletely cracked does not fragment, but $\triangle E_b/W$ is greater than 0.20kJ/g, where W is sample mass(g).

No propagation: all other observation may be reduced.

If the assessment of deflagration is difficult, the sample mass and the variable initiator test conducted. In addition, detonation or deflagration can be determined by comparison with energy of shock wave per unit of mass ($\triangle E_s/W$).

R7 Examples of 50/60 steel tube test underwater

The results of the 50/60 steel tube test underwater are listed in Table 3.41.

3.8.6 Variable sample mass test with the MKIII ballistic mortar[55, 56)

(1) Name of the test method

Variable sample mass test with the MKIII ballistic mortar.

(2) Property evaluated

Propagation of deflagration : Detonatable substances cannot be tested because the apparatus will be broken.

(3) Apparatus and materials

(a) MKIII ballistic mortar

The MKIII ballistic mortar is the same mortar used in the test with variable initiators.

(b) Sample

The sample vessel in the variable sample mass test is made of a thin polyethylene tube with a diameter of 23 mm. The bottom is closed by adhesive tape. The initiating explosive with a No.6 electric detonator and 0.6 g of PETN is inserted into the inner tube used in the variable initiator test. A sample vessel assembly is shown in Fig.3.138.

(4) Procedure

Charge of 10, 20, or 30g of sample are is inserted into a polyethylene tube with a diameter of 23 mm, the bottom of which is sealed with adhesive tape. The inner polyethylene tube with 0.6g PETN is inserted into the top of a polyethylene bag and that bag is fastened. A No.6 electric detonator is inserted into the inner tube, the sample vessel assembly is placed in the ballistic mortar bore, and the 2kg projectile is attached. The leg wire of the detonator is connected to the firing circuit, the charge is fired and the length of swing is measured.

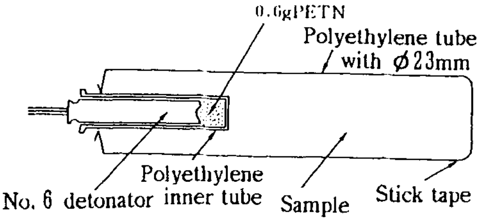


Fig. 3.138 Sample set of variable sample test

(5) Evaluation of results

The method for measuring the net swing length is the same as that used in the variable intiator test. The swing lengths are plotted against the weight of the sample, and the curve of the net swing length is shown.

(6) Assessment of results

Propagation of deflagration : The length of the swing increases with sample weight mono tonically.

Non-propagation of deflagration : The length of the swing increases with sample weight, but the increase stops halfway.

(7) Example

The example is shown in table 3.42.

Table 3.42 Test results for detonation-propagation: Net length of swing of mortar

Substances	Sample mass (g)			Detonation-propagation
	10	20	30	
BPO	88	151	217	±
10% water BPO	98	148	209	±
20% water BPO	88	142	181	±
25% water BPO	76	76	106	−
DTBO	127	93	165	±
TBPB		216	287	±
LPO	18	19	37	−
DHPBO	32	13	21	−
BPEH	87	157	214	±
MSP	11	12	13	−
BPIPB	77	97	107	±
H48	12	10	12	±
ADCA	54	32	33	−
AIEN	79	98	126	±

(8) Evaluation of tests with variable sample mass with the MKIII ballistic mortar.

(a) Relationship between the length of swing and the sample mass

The typical relationship between the length of swing and the sample weight is shown in Fig.3.139.

BPO 100 propagates the explosion completely; the length of swing increases linearly with the sample weight. In the case of a small mass of TBPB, the rate of increase of the net swing length against the sample weight is large, but when the sample weight exceeds 10g, the rate of increase decreases and becomes constant. The difference between the two tendencies can be explained as follows. In an explosion with a No.6 electric detonator and 0.6 g PETN, BPO 100 does not decompose with a strong explosive power, but it produces a self sustaining explosion. On the other hand, TBPB decomposes with a stronger explosive power than a self sustaining explosion within the range of sample weights up to about 10g. If the sample weight exceeds this range, TBPB experiences a self−sustaining explosion. Therefore, to know the power of self−sustaining explosions, one needs to examine the range of increase for the length of swing against sample weight for samples over 10g. The ballistic pendulum test shows that for TBPB the graph of the swing length is similar to DTBO, though this may be due to the stronger initiating power of TBPB than BPO 100.

For DTBO, a large scatter is observed in the data because the sensitivity of DTBO is so low that a No.6 electric detonator plus 0.6 g PETN is not enough to initiate DTBO. DTBO explodes completely if initiated by a booster of 5g PETN in the ballistic pendulum test [68] .

For BPO 75, the increase of the swing length vs. sample weight levels off between the 10 and 15 g sample. A longer swing length is observed for the 20g sample. Therefore, BPO 75 may propagate an explosion if a larger quantity of booster and a larger diameter of sample are used. However, BPO 75 does not propagate explosions under the conditions using a 20g booster and a sample 50 mm in diameter in the ballistic pendulum test [68] .

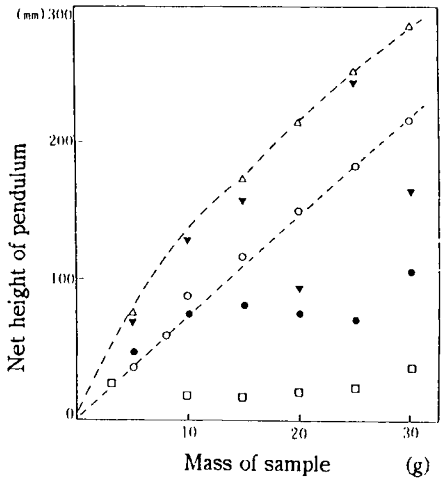


Fig. 3. 139 Examples of net height of pendulum vs mass of sample

○: BPO100, ●: BPO75

△: TBPB, ▲: DTBO, □: LPO

For LPO, the swing length initially increases with sample weight but also levels off. LPO does not propagate an explosion. Therefore, all substances which are judged for non-sensitivity in this test do not propagate an explosion.

(b) Assessment criteria for the propagation of an explosion and propagation of an explosion of organic peroxide

We propose the fowllowing criterion based on our evaluations. The propagation of explosions was clearly confirmed by the swing length of 10, 20 and 30g samples.

The propagation of explosions for organic peroxides was evaluated by the swing length corresponding to

$$d^{s}_{30} - d^{s}_{20} \geqq 0.2\, d^{s}_{20}$$

and to $d^{s}_{20} - d^{s}_{10} \geqq 0.4\, d^{s}_{10}$.

However, this propagation is not a propagation of detonation but more likely a propagation of deflagration. Whether detonation was propagated or not can be judged from the results of the BAM 50/60 steel tube test under sand or water. All peroxides examined in this section do not detonate. The results of the evaluation of propagation of an explosion with a ballistic mortar are shown in Table 3.42. When these results are compared with the results of the ballistic pendulum test, both results are the same except for two substances. The results for DTBO do not correspond because is has a low sensitivity. If the sample were larger, the results would have been the same. As BPO 80 is found to be a boundary substance in the ballistic pendulum test, it may be assumed that BPO 80 can propagate an explosion. Therefore, the propagation of the explosion for almost all organic peroxides can be evaluated by using the MKIII ballistic mortar. Regarding substances of low sensitivity, one may examine propagation with larger initiator masses.

3.8.7 Testing sample of variable mass using the ballistic pendulum (T)

T1 Name of test method

Variable sample mass test using the ballistic pendulum.

T2 Property to be evaluated

Propagation of deflagration. (This method should not be used for substances which detonate because the apparatus may break.)

T3 Apparatus and materials

T3.1 Ballistic pendulum

Two kinds of ballistic pendulum as shown in Figure 3.140 and 3.141 may be used in Japan. The former, owned by Nippon Kayaku Co., Ltd., is based on Japanese Industrial Standards (JIS) and the latter, owned by Nippon Oil and Fats Co., Ltd., is made from a cannon barrel like the ballistic pendulum at the Buxton Laboratory of HSE in Great

Britain.

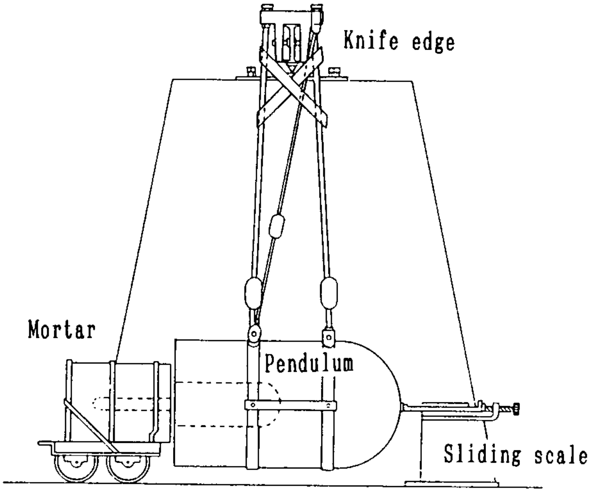


Fig. 3.140 The ballistic pendulum in the Asa factory of Nippon Kayaku
The holl diameter is 55 mm and the depth is 550 mm

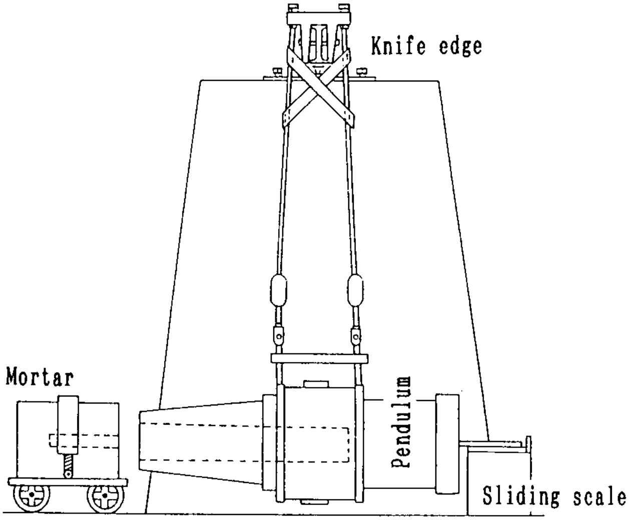


Fig. 3.141 The ballistic pendulum in the Taketoyo factory of Nippon Oil & Fats
The holl diameter is 50 mm and the depth is 480 mm

T3.2 Test samples

100, 200 and 300g of test sample are put in a 50mm diameter polyethylene tube and then initiated with a booster composed of a No.6 electric cap and 20g of PETN in a 30mm diameter polyethylene tube. 1kg of sand cartridge is inserted behind the test sample to better confine it and the mortar is set in a position close to the pendulum. (The distance between mortar and pendulum should be 15 mm.)

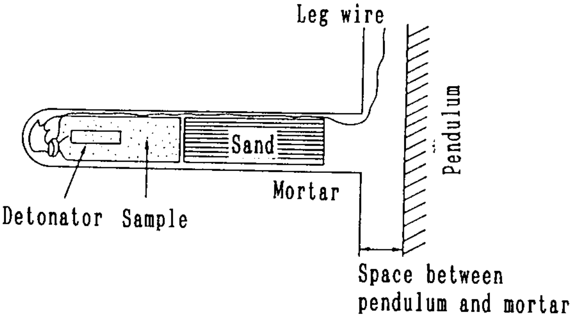


Fig. 3.142 The charged sample

T4 Operating procedure

A known mass of test sample is put in the 50mm diameter polyethylene tube. A booster composed of a No.6 electric cap and 20g of PETN in a 30mm diameter polyethylene tube is also put in the tube. This cartridge is inserted into the back of the mortar bore. One sand cartridge is inserted behind the test sample and the mortar is moved 15mm from the pendulum. The test sample is initiated and the swing of the pendulum is measured.

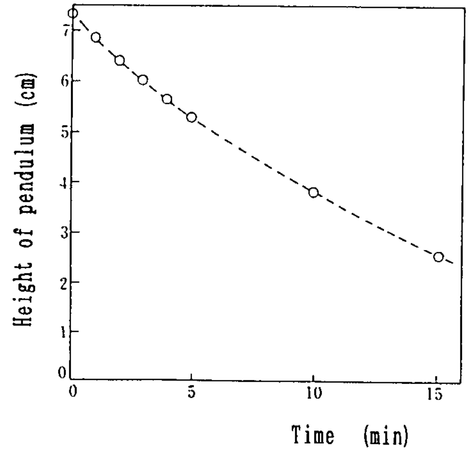


Fig. 3.143 The reduction in the swing of the ballistic pendulum

T5 Evaluation of test results

A number of tests at various sample weights should be conducted. If the swing of pendulum increases with sample weight, the process is considered to be propagation.

T6 Assessment of test results

Propagation of deflagration

Propagation:

$$(d^{s}_{300} - d^{s}_{200})/d^{s}_{200} \geqq 0.2 \text{ and } (d^{s}_{200} - d^{s}_{100})/d^{s}_{100} \geqq 0.4$$

where d^{s}_{m} means the net swing length of pendulum with a given mass(g) of the test sample.

No propagation : substances which do not satisfy the above conditions.

3.8.8 Basic feature of the test method using the ballistic pendulum 68)

(1) Basic features of the ballistic pendulum

(a) The pendulum swing.

Figure 3.143 shows data actually measured with the ballistic pendulum from the Asa factory of Nippon Kayaku Co., Ltd. When these data are treated, the following equation results. The swing reduction of the pendulum with resistance is less than in the case of the ballistic mortar. The maximum observation error in each swing is 0.8 and the average observation error is about 0.2.

$d=a \cdot \exp(-1.06 \times 10t) \cdot \sin(2\pi t/3.05)$

where t is time and the swing period is 3.05 seconds.

(b) Relationship between weight of charge and pendulum swing

Katsuki et al. showed that the pendulum swing varies linearly with the charge weight when they tested the ammonium explosives with the ballistic pendulum 79) . To determine if this relationship applies for other explosive substances, PETN, TNT, black powder and DPT were tested with variable sample weights. Figure 3.144 shows that the relationship between pendulum swing and sample weight for PETN is satisfactorily linear when the tests are carried out without tamping. This relation is similar to the test results with MKIII ballistic mortar. In the case of TNT by removing the surrounding air space with polyethylene powder and glycerin liquid, Figure 3.144 shows that the relationship is not always linear. Figure 3.145 shows the relation between pendulum swing and sample weight for certain explosive substances having propagation properties. The relation between pendulum swing and sample weight is not a simple one. One tentative explanation for this behavior is that the explosive power of substances that propagate weakly as shown in Figure 3.145 is divided two sections. One is the explosive power supported by powerful PETN booster, and the other is the explosion supported by the self−sustained explosion of the sample itself. When the self−sustained explosion power is studied, the data for sample over 100g should be used for comparison to cancel the effect of the booster. However, as you will recognize in a later discussion, it is difficut to make absolute estimations of explosive power, because the pendulum swing is affected by the charging conditions of sample. The swing caused by black powder shows complicated behavior, and detailed investigations are required to explain this phenomena correctly.

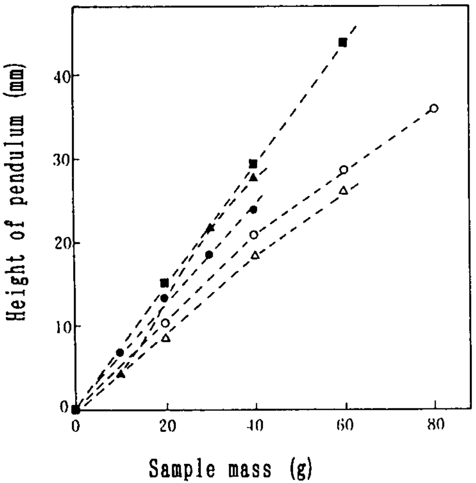


Fig. 3.144 The swing length of the pendulum with various sample weights without tamping

■:PETN
▲:PETN+300 g glycerin
●:PETN+150 g calcium stearate
△:TNT+300 g glycerin
○:TNT+150 g calcium stearate

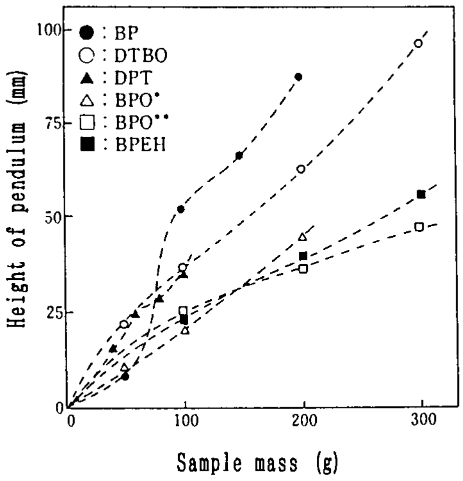


Fig. 3.145 The net–swing length of the pendulum with various sample weight for substances that propagate explosively

* Data from Nippon Kayaku Co.
** Data from Nippon Oil & Fat Co.

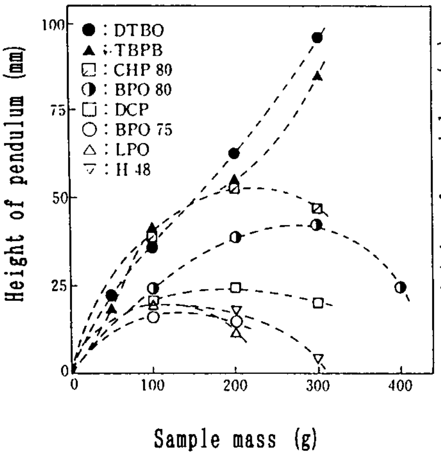


Fig. 3.146 The net–swing length of the pendulum at Nippon Kayaku with variable sample weights of organic peroxides

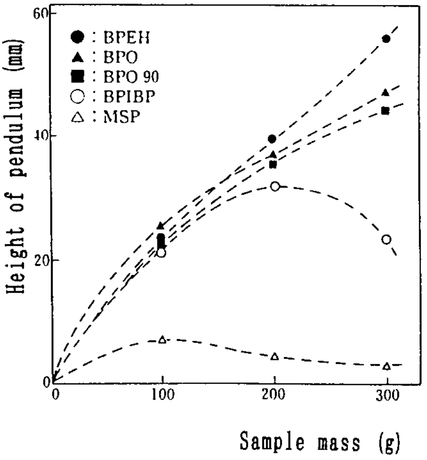


Fig. 3.147 The net–swing length of the pendulum at Nippon Oil and Fats with variable sample weights for organic peroxides

(2) Propagation test for organic peroxides

Propagation test results for 9 kinds of organic peroxides were reported by reseachers from various countries at the Seminar of Test Method for Organic Peroxides held on 9 to 11 in October of 1984 [52]. Test results for these 9 substances and other organic peroxides are shown in Figure 3.146 and 3.147.In standard tests, 20g of PETN was used as booster. Though benzoyl peroxide (BPO) was tested with the normal test method, we recommend that small sample tests should be carried out for examination of propargation and large volume tests should be avoided as much as possible on extremely sensitive substances like as BPO to maintain the operator's safety.

In these test methods we determined a tentative standard for judging propagation as follows. When the net increase is given by subtracting the swing with 200g of sample from that with 300g of sample is more than 20% of that with 200g and the net increase from the swing with 100g to 200g of sample is more than 40% of that with 100g of sample, the test sample was judged as capable of propagation. The test samples judged to be detonated with other test methods are classified as detonation propagation (+) and those deflagrated are classified as deflagration propagation (±).

Among the organic peroxides tested, BPO (pure), BPO (containing 10% water), TBPB, DTBO and BPEH were judged to propagate explosions by this test. BPO (containing 20% water) is on the border line of explosion propagation. While the charge weight was increased from 200g to 300g, the net increase of swing did not exceed 20% of the swing with 200g of BPO(20% water). When the charge weight was 400g, the swing was shorter than the swing value with 300g. When the charge weight was increased from 100g to 200g, however the net increase of swing was 63%. The samples which show more than 20% net increase when the charge weight is increased from 100g to 200g, but no increase when the charge weight is increased of more than 200g were BPIBP and CHP80%. DTBO showed propagation, but DTBO−GMB diluted with approximately 20% glass micro balloons showed no propagation. These results indicate that the effects of diluting the test substance with glass spheres to decrease propagation are greater than the effects of increasing propagation by the addition of microsphere. BPO75 (containing 25% water), CHP, LPO, MSP and H48 do not demonstrate net explosion. It is well−known that pure BPO is a highly dangerous substance, but BPO containing 25% water can be safety in the present commercial market. The results of this investigation indicate that this is adequate precaution.

(3) Comparison between the test results from this method and from other test methods

As this test method can detect the explosion ratio, it is possible to determine propagation more quantitatively than with the 50/60 iron tube test, the 50/70 iron tube test and the US gap test. Also the MKIII ballistic mortar can be used for a similar test, but the limit for the MKIII ballistic mortar is a 25mm diameter test sample. Meanwhile the MKIII ballistic mortar has the advantage to beening able to test with a small mass of sample. In this chapter the points at issue for each test method are considered by comparing the results from this method and those from other test methods. Table 3.43 shows such a comparison.

The differences between the 50/60 steel tube test and the ballistic pendulum for the propagation test method are as follows. By the ballistic pendulum method samples which do not detonate but propagate violent deflagration are judged to propagate. In contrast the steel tube is not broken entirely by propagation of violent deflagration, only by propagation of detonation, in 50/60 steel tube test. The samples which propagate violent deflagration are not judged to propagate by the 50/60 steel tube test. Pure BPO is a substance which has caused many accidental explosions, but it has not been clear up to now whether this substance detonates or deflagrates. The BAM 50/60 steel tube is not broken into fragments but is split completely and has cracks at both ends with BPO. BAM judges it to detonate. Tanaka and Matsuyama measured the detonation velocity of BPO in a polyethylene tube using modified optical fiber. As the result of this measurement they observed a progressing deflagration wave with a velocity of 500m/sec after a detonation wave of 2,000 m/sec [80]. Pure BPO, dried nitrocellulose and black powder do not detonate but deflagrate violently. They have caused many accidents. One reason for accidents with these substances is that they burn violently and explosively. Another reason is that they have high sensitity. Accordingly it is safer to classify substances which propagate violent deflagration and also have high sensitivity as high dangerous substances. For such evaluations it seems to be effective to carry out the propagation test using the ballistic pendulum combined with a shock sensitivity test using the ballistic mortar.

The TNO 50/70 steel tube test has the problem that the steel tube is not broken completely by a weak detonation because it is too strong. Meanwhile it has the advantage that it distinguishes detonation by detonation velocity measurements using the resistance−probe method. However, accurate detonation velocity cannot be measured easily with this test for low velocity detonations. At the present time we consider that it is important for the evaluation of the explosion danger of unstable substances to distinguish substances which make a dent in the witness plate in the U.S. gap test from the substances which do not make a dent but which have deflagration propagation properties as judged by the ballistic pendulum.

(4) Static explosive power with the ballistic pendulum

The ballistic mortar test and the ballistic pendulum test are the test methods of choice for the static explosion power of explosives. When explosive substances are exploded in a mortar, a portion of generated energy is absorbed in the mortar as shock waves and another portion of energy is released to the outside as heat. An additional portion of energy swings the mortar or pendulum. When the same weight of the same substances are used, swing values change in obedience to the structure of the mortar or the charging conditions. One reason for this is that the ratio among the energy release forms changes with the mortar structure and charging method. For instance, in the case of MKIII ballistic mortar the ratio of shock waves fading away into mortar is great, because the samples are charged tightly into the mortar. In the case of the typical ballistic pendulum test the shock waves generated by the explosion are reflected by the mortar wall and change into gas expansion energy because the space between sample and mortar is relatively large. Some experiments show the resulting explosion energy (gas expansion energy) of the ballistic pendulum is increased, when the space is made smaller. The difference between the static power ratio of 1.2 of PETN to TNT measured with the MKIII ballistic mortar and that of 1.4 with the ballistic pendulum is explained this way. The sample substances which will be tested for propagation properties by these test methods are explosive substances on the border line between detonation and deflagration. There are some problems with making TNT the standard substance in these cases. TNT is a high detonation velocity explosive and has higher energy released as shock waves. As the observed gas expansion energy changes severely with the mortar structure and charging method for these high explosives, TNT is not adequate as standard substance. We selected 100%BPO as the standard substance because it has propagates reliably and scarcely releases shock waves, and we calculated its explosion power (EPBP) with the ballistic pendulum for propagation from the following equation. However, as 100%BPO is highly sensitive substance, it is preferable to select another pure substance with lower sensitivity as the standard substance.

$$\mathrm{EPBP} = 100 \times (d^{s}_{300} - d^{s}_{100})/(d^{BPO}_{300} - d^{BPO}_{100})\ (\%)$$

where d is pendulum swing value, superscript side "s" is sample and BPO is 100% BPO, subscript "300" or "100" are sample weights in grams. Table 3.44 shows these test results along with the test results done by the MKIII ballistic mortar.

Table 3.43 Comparison of the test methods for propagation of explosion between ballistic pendulum and others.

Substances	Ballistic Pendulum	BAM 50/60 Steel tube4)	TNO 50/70 Steel tube4)	US gap	MKIII Ballistic Motar
BPO	±	+		−	±
BPO90	±				±
BPO80	−				±
BPO75	−	−	±		−
TBPB	±	±	−		±
DTBO	±	−			−
DTBO-GMB	−				
CHP80	−	−			−
DCP	−	±			−
LPO	−	−	±		−
BPEH	±		−		±
DCHPDC			+		
DCHPDC90			+		
DCPDC		−			
CMPDC		−			
DMPDC42		−			
H48	−				−
DPT	+	+			
MSP	−				−
BPIPB	−				−

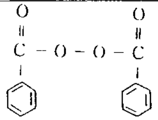
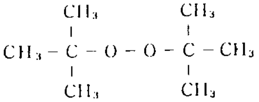
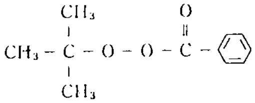
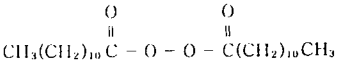
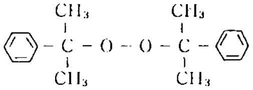
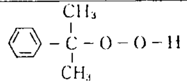
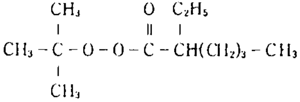
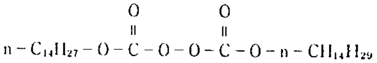
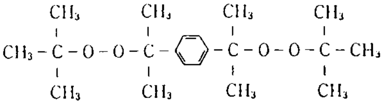
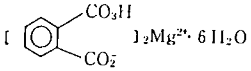
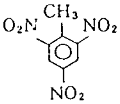
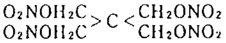
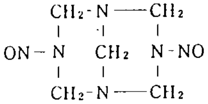
+	propagation of detonation
±	propagation of deflagration or partial reaction
−	no propagation of explosion

Table 3.44 The static explosion power of organic peroxides with the ballistic pendulum and the ballistic motar (The swing length of BPO is taken as 100%)

Organic peroxides	Ballistic pendulum in Nippon Kayaku	Ballistic pendulum in Nippon Oil and Fats	Ballistic motar MKIII
BPO	100	100	100
BPO90	−	100	86
BPO80	−	−	72
DTBO	135	−	127*
TBPB	101	−	125
BPEH	−	149	99

* calculated value

Table 3.45 The name, symbol and structure of organic peroxides

	Substance Name	Symbol	Structure
	Dibenzoyl peroxide	BPO	
	containing 10% water	BPO90	
	containing 20% water	BPO80	
	containing 25% water	BPO75	
	Di-tert-butyl peroxide	DTBO	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$
	tert-Butyl peroxibenzoate	TBPB	
	Dilauroyl peroxide	LPO	 $CH_3(CH_2)_{10}\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3$
	Dicumyl peroxide	DCP	
	Cumyl hydroperoxide (20% Isopropylbenzene)	CHP80	
	tert-Butyl peroxy-2-ethyl-hexanoate	BPEH	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{O}{\overset{\|}{C}}-\overset{C_2H_5}{CH}(CH_2)_3-CH_3$
	Dimyristyl peroxydicarbonate	MSP	 $n-C_{14}H_{27}-O-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-O-n-CH_{14}H_{29}$
	α,α'-Bis(tert-butyl peroxi-p-isopropyl)benzene	BPIPB	
	Magnesium monoperoxi-phthlate, hexahydrate powdered	H48	
	Trinitrotoluene	TNT	
	Black Powder(gun powder)	BP	
	powdered PETN	PETN	 $\begin{matrix}O_2NOH_2C\\O_2NOH_2C\end{matrix}>C<\begin{matrix}CH_2ONO_2\\CH_2ONO_2\end{matrix}$
	"Cherry" Dynamite	—	
	N,N'-Dinitroso-pentamethylene tetramine	DPT	

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Chapter 4

HAZARDOUS MATERIALS AND CONCRETE TESTING METHODS APPLIED TO THEM

Classification and methods for the evaluation of hazardous materials are briefly described in Section 1.3. Testing methods for reactive chemical substances are described in Chapter 3. This chapter discusses what methods should be actually combined for testing materials mainly under the Fire Protection Law and for voluntary in–firm confirmation.

This Chapter details oxidizing solids, which are typically reactive with other materials. At the end of this chapter reactive chemical substances (oxidizing, spontaneously combustible, water–hazardous, unstable, explosive substances) are classified caccording to Bretherick. For the hazardous materials [19] under the revised Fire Protection Law, reference should be made to Jiromaru's commentary [20] .

4.1 Oxidizing Solids

4.1.1 Uses, locations, production and regulations of oxidizing solids [1]

Oxidizing agents are substances which are apt to discharge oxygen.

The exothermic reaction of discharged oxygen with combustible substances has been utilized for pyrotechnic products, including gunpowders, explosives and fireworks.

The chemical activity of oxidizing agents is important in many products such as fertilizers, herbicides, bleaching agents, disinfectants, germination regulating agents, polymerization initiating agents, neutralizing agents, and chemical reaction reagents. Oxidizing agents are used also as oxygen generating agents. Some oxidizing agents have intrinsic ignition or explosion hazards and are also hazardous when mixed with other substances. To prevent accidents, some oxidizing agents are legally controlled in Japan by the Fire Prevention Law, Labor Safety and Sanitary Law, and Regulations for Marine Transportation and Storage of Hazardous Materials. Some oxidizing agents are specified internationally as hazardous materials by the United Nation International Committee of Experts on the Transportation of Dangerous Goods.

In 1979 the Fire Department in Tokyo carried out a fact–finding survey of chemical and pharmaceutical products. This survey was conducted in all business establishments, research laboratories, universities and colleges as well as selected hospitals, public health centers, seniorhigh schools, juniorhigh schools and primary schools in Tokyo which stored chemical and pharmaceutical products as part of measures for preventing earthquake disaster. Survey items included: name of product and quantity contained in each bottle; method of storage, such as composition of container and height of shelf; construction of building; and protection of shelves against falling.

This survey revealed that hundreds of oxidizing agents exist in Tokyo (Table 4.1). Table 4.2 lists substances specified as oxidizing materials by the United Nations. Table 4.3 shows the production of oxidizing agents in Japan. Table 4.12 (the end of Chapter 4) shows substances [18] listed in Bretherick's book [17] .

Table 4.1 Oxidizing Agents in Tokyo According to Survey Conducted by the Fire Department of Tokyo

Substances	Molecular form	$\triangle Hf^\circ$ [kcal/mol]	Index No.
Bleaching powder	$Ca\ Cl_2O_2$	-178.6	1004000
Potassium hypochlorite	$K\ Cl\ O$	-85.4	1005010
Bismuth hypochlorite(S)	$Bi\ Cl\ O$	-87.3	1005040
Chlorous acid	$H\ Cl\ O_2$	-12.41	1008000
Chloric acid	$H\ Cl\ O_3$	-23.4	1010000
Ammonium chlorate	$N\ H_4\ Cl\ O_3$	-55.4	1010010
Potassium Chlorate(S)	$K\ Cl\ O_3$	-93.5	1010020
Sodium Chlorate	$Na\ Cl\ O_3$	-65.73	1010030
Calcium chlorate	$Ca\ Cl_7O_6$	-164.0	1020100
Barium Chlorate(S)	$Ba\ Cl_2O_6$	-182.39	1010110
Rubidium chlorate(S)	$Rb\ Cl_2O_3$	-93.8	1010120
Zinc chlorate	$Zn\ Cl_2O_9$	-83.3	1010130
Silver Chlomate	$Ag\ Cl\ O_3$	-5.73	1010140
Iodic acid	$H\ I\ O_3$	-55.0	1010300
Ammonium perchlorate	$N\ H_4\ Cl\ O_4$	-69.42	1020010
Potassium Perchlorate(S)	$K\ Cl\ O_4$	-103.6	1020020
Sodium Perchlorate	$Na\ Cl\ O_4$	-91.479	1020030
Barium Perchlorate(S)	$Ba\ Cl_2O_8$	-191.21	1020080
Calcium perchlorate	$Ca\ Cl_2O_8$	-176.08	1020090
Cobalt perchlorate(S)	$Co\ Cl_3O_{12}$	-132.29	1020100
Rubidium perchlorate(S)	$Rb\ Cl\ O_4$	-103.87	1020120
Strontium perchlorate(S)	$Sr\ Cl_2O_8$	-182.31	1020130

Substances	Molecular form	ΔHf° [kcal/mol]	Index No.
Magnesium Perchlorate	$Mg\ Cl_2O_8$	-135.97	1020160
Magnesium perchlorate	$Mg\ Cl_2O_{14}H_{12}$	-584.44	1020161
Lithium perchlorate	$Li\ Cl\ O_4$	-90.99	1020170
Sodium perchlorate	$Na_2Cr\ O_4$	-317.59	1020320
Sodium perchlorate ($4H_2O$)	$Na_2Cr\ O_8\ H_8$	-601.29	1020321
Ferrous perchlorate	$Fe\ Cl_2O_8$	-83.1	1020340
Calcium perchlorate	$Ca\ O_2$	-157.4	1030100
Potassium peroxide	$K_2\ O_2$	-67.7	1030110
Hydrogen peroxide(L)	$H_2\ O_2$	-44.84	1030130
Hydrogen Peroxide (30%)	$H_{20}O_{12}$	-639.84	1030131
Barium peroxide	$Ba\ O_2$	-151.6	1030140
Sodium Peroxide	Na_2O_2	-122.66	1030150
Ammonium Nitrate	$N_2\ H_4\ O_3$	-87.371	1040010
Potassium Nitrate(S)	$K\ N\ O_3$	-117.76	1040020
Sodium Nitrate	$Na\ N\ O_3$	-111.54	1040030
Nitroguanidine(S)	$C\ H_4\ N_4\ O_2$	-22.1	1040040
Silver nitrate(S)	$Ag\ N\ O_3$	-29.43	1040050
Lithium Nitrate(S)	$Li\ N\ O_3$	-115.28	1040060
Barium Nitrate	$Ba\ N_2\ O_6$	-273.0	1040070
Lead Nitrate	$Pb\ N_2\ O_6$	-107.35	1040080
Strontium Nitrate(S)	$Sr\ N_2\ O_6$	-233.25	1040090
Calcium Nitrate(S)	$Ca\ N_2\ O_6$	-226.0	1040100
Magnesium Nitrate(S)	$Mg\ N_2\ O_6$	-188.72	1040110
Uranyl Nitrate(S)	$U_2\ N_2\ O_6$	-329.2	1040120
Manganese Nitrate(S)	$Mn\ N_2\ O_6$	-166.32	1040130
Copper Nitrate(S)	$Cu\ N_2\ O_6$	-73.4	1040150
Cesium Nitrate(S)	$CS\ N\ O_3$	-118.11	1040130
Radium nitrate(S)	$Ra\ N_2\ O_6$	-237.0	1040190
Rubidium nitrate(S)	$Rb\ N\ O_3$	-117.04	1040200
Zinc nitrate	$Zn\ N_2\ O_6$	-115.6	1040230
Mercuric Nitrate	$Hg\ N_2\ O_6$	-58.4	1040240
Nickel (II)nitrate	$Ni\ N_2\ O_6$	-99.2	1040250
Nickel (II)nitrate ($3H_2O$)	$Ni\ N_2\ O_7\ H_6$	-316.99	1040251
Nickel (II)nitrate ($6H_2O$)	$Ni\ N_2\ O_{12}H_{12}$	-528.6	1040252
Cobalt (II)nitrate	$Co\ N_2\ O_6$	-100.5	1040270
Aluminum nitrate ($6H_2O$)	$Al\ N_3\ O_{15}H_{12}$	-681.9	1040290
Ammonium nitrate(S)	$N_2\ H_4\ O_2$	-63.1	1045030
Silver Nitrate(S)	$Ag\ N\ O_2$	-10.01	1045040
Potassium permanganate	$k\ Mn\ O_4$	-194.4	1050010
Sodium permanganate	$Na\ Mn\ O_4$	-186.8	1050020
Calcium permanganate	$Ca\ Mn_2O_8$	-377.57	1050030
Magnesium permanganate	$Mg\ Mn_2O_8$	-358.21	1050050
Silver dichromate(S)	$Ag_2Cr_2O_7$	-170.15	1060040
Diarsenic pentoxide(S)	As_2O_5	-218.6	1090030
Gold (III)oxide(S)	Au_2O_3	19.3	1090040
Chlorine monoxide(G)	$Cl\ O$	24.352	1090160

Substances	Molecular form	△Hf° [kcal/mol]	Index No.
Dichlorine monoxide(G)	Cl_2O	21.02	1090190
Dichlorine heptoxide(G)	Cl_2O_7	56.93	1090200
Copper (I)oxide(S)	CuO	-37.267	1090200
Difluorine monoxide(S)	F_2O	5.5	1090260
Iron (III)oxide(S)	Fe_2O_3	-196.5	1090270
Iron (II)+Iron (III)oxide(S)	Fe_3O_4	-267.0	1090280
Germanium dioxide(S)	GeO_2	-129.0	1090320
Hydrogen peroxide(L)	H_2O_2	-44.84	1090330
Mercury (I)oxide(S)	Hg_2O	-21.5	1090350
Potassium superoxide	KO_2	-67.7	1090360
Lithium oxide(S)	Li_2O	-151.8	1090380
Magnesium oxide(S)	MgO_2	-140.9	1090410
Manganese (III)oxide(S)	Mn_2O_3	-232.1	1090440
Trimanganese tetraoxide	Mn_3O_4	-331.4	1090450
Molybdenum dioxide(S)	MoO_2	-139.5	1090460
Dinitrogen monoxide(G)	N_2O	19.49	1090500
Dinitrogen trioxide(G)	N_2O_3	20.0	1090510
Dinitrogen pentoxide(G)	N_2O_5	3.6	1090530
Dinitrogen pentoxide(S)	N_2O_5	-10.067	1090540
Sodium superoxide(S)	NaO_2	-61.9	1090550
Disodium dioxide(S)	Na_2O_2	-120.6	1090570
Niobium dioxide(S)	NbO_2	-189.5	1090590
Diniobium pentoxide(S)	Nb_2O_5	-454.0	1090600
Dilead dioxide(S)	PbO	-51.22	1090660
Lead (II)oxide(S)	Pb_3O_4	-175.6	1090670
Praseodymium (III)oxide	Pr_2O_3	-434.0	1090690
Plutonium dioxide(S)	PuO_2	-246.0	1090700
Rubidium oxide(S)	Rb_2O_2	-101.7	1090720
Rubidium (III)oxide(S)	Rb_2O_3	-116.7	1090730
Rubidium tetroxide(S)	Rb_2O_4	-126.2	1090740
Rhodium monoxide(S)	RhO	-23.9	1090750
Rhodium (III)oxide(S)	Rh_2O_3	-68.3	1090770
Ruthenium oxide(S)	RuO_2	-52.5	1090780
Sulfur trioxide(S)	SO_3	-107.45	1090800
Antimony dioxide(S)	SbO_2	-96.0	1090830
Antimony (III)oxide(S)	Sb_2O_3	-167.0	1090840
Antimony (V)oxide(S)	Sb_2O_5	-215.0	1090850
Scandium (III)oxide(S)	Sc_2O_3	-410.0	1090860
Silicon dioxide(S)	SiO_2	-205.4	1090850
Tin (II)oxide(S)	SnO_2	-138.8	1090900
Strontium (II)oxide(S)	SrO_2	-153.6	1090920
Technetium (II)oxide(S)	TcO_2	-103.5	1090930
Technetium (III)oxide(S)	TcO_3	-129.0	1090940
Ditechnetium heptaoxide	Tc_2O_7	-266.14	1090950
Tellurium (II)oxide(S)	TeO_2	-77.69	1090960
Titanium dioxide(S)	TiO_2	-218.0	1090980

Substances	Molecular form	△Hf° [kcal/mol]	Index No.
Titanium (V)oxide	Ti_3O_5	-584.0	1091000
Dithallium trioxide(S)	TlO_3	-34.5	1091020
Uranium dioxide(S)	UO_2	-270.0	1091030
Uranium trioxide(S)	UO_3	-302.0	1091040
Vanadium (III)oxide(S)	V_2O_3	-290.0	1091060
Vanadium tetraoxide(S)	V_2O_4	-344.0	1091070
Tungeten dioxide(S)	WO_2	-134.0	1091090
Zirconium dioxide(S)	ZrO_2	-258.2	1091130
Diyttrium trioxide(S)	Y_2O_3	-425.0	1091160
Chromium (VI)oride	CrO_3	-140.83	6070010
Potassium chlorite	$KClO_2$	-76.2	7010010
Sodium Chlorite	$NaClO_2$	-72.65	7010020
Ammonium bromate	KH_4ErO_3	-51.7	7010040
Potassium Bromate	$KBrO_3$	-90.13	7010060
Silver bromate	$AgBrO_3$	-6.5	7010070
Sodium Bromate	$NaBrO_3$	-83.83	7010080
Barium bromate	$BaBr_2O_6$	-179.89	7010100
Zinc iodate	$ZnIr_2O_6$	-142.6	7010120
Ammonium iodate	NH_4IO_3	-92.2	7010130
Potassium Iodate	KIO_3	-119.83	7010140
Calcium iodate	CaI_2O_6	-239.6	7010150
Silver Iodate	$AgIO_3$	-40.9	7010160
Barium iodate	BaI_2O_6	-245.5	7010180
Sodium Iodate	$NaIO_3$	-115.15	7010200
Ammonium Dichromate	$N_2H_8Cr_2O_7$	-431.8	7010220
Potassium Dichromate	$K_2Cr_2O_7$	-485.9	7010230
Sodium Dichromate	$Na_2Cr_2O_7$	-463.4	7010250
Calcium dichromate	$CaCr_2O_7$	-171.8	7010260
Potassium Persulfate	K_2CrO_4	-440.6	8050300
Potassium Chromate	K_2CrO_4	-320.2	8140070
Sodium Chromate	Na_2CrO_4	-320.8	8140070
Sodium Nitrate	$NaNO_2$	-85.9	8140030

Note 1: Substances used as samples for the improved steel dish test are capitalized.

Note 2: In case the first digit of the index No. is 1, the substance belongs to the first group of hazardous materials according to the Fire Protection Law.

Table 4.2 Oxidizing Substances (Class 5.1) according to United Nations

Cations	Alkaline metal					Alkaline earth metal					Typical elements				Transition elements								NOS
Substances	HN_4	Li	Na	K	Cs	Be	Mg	Ca	Sr	Ba	Al	Tl	Pb	Zn	Cr	Mn	Fe	Ni	Cu	Ag	Zr	Nb Pr	
Chlorates			●	●			●	●	●	●		●		●					●				●
Perchlorates	●	□	●	●			●	●	●	●			●										●
Peroxides		●	◎	◎			●	●	●	●			○	●	●								●
(Superoxides)			◎	◎																			
(Persulfates)	○		○	○																			
(Percabonates)			○																				
Nitrates	□	○	○	○	○	●	○	○	○	●	○	▲	●	●	○	○	○	○		●	○	○	●
Permanganates	○$^{4)}$		●	●				●		●				●									●
Chlorites			●					○										○					●
Bromates			●	●			●			●				○									●
Iodates																							
Dichromates	●																						
Hypochlorites		●						●		●													
Nitrites			○	●																			●

Note 1 ● denotes a substance whose content is specified. Packing groupNote 2

▲ denotes a substance whose subsidiary risks are spacified as 5.1 I ◎

Note 3 □ denotes a substance listed in other class. II ●

Note 4 Transportation of ammonium permanganate requires special permission. III ○

Table 4.3 Production of Oxidizers (in 1984)

Classification	Substances	Production (t)	Uses
Chlorates	Sodium chlorate	31,785^{*1}	Herbicide, reagent, oxygen generating agent
	Potassium chlorate	785^{*2}	Explosives, match, herbicide, fireworks
Perchlorates	Sodium perchlorate	(1,600)^{*2}	Oxidizing agent
	Potassium perchlorate	606^{*2}	Fireworks, oxidizing agent
	Ammonium perchlorate	900^{*3}	Solid propellant, carlit

Peroxides (inorganic)	Hydrogen peroxide (100% conversion)	94,736*1	Bleaching agent, pharmaceuticals
	Sodium persulfate	4,400*3	Bleaching agent, analyzing reagent
	Potassium persulfate	3,200*3	Catalyst, bleaching agent, reagent
	Ammonium persulfate	4,500*3	Polymerizing agent, oxidizing bleaching agent
	Sodium perborate	(1,000)*2	Oxidizing bleaching agent, washing and sterilizing agent
	Sodium peroxide	2.9*2	Reagent, raw material
	Potassium peroxide	(Import)	Oxidizing agent
	Calcium peroxide	(100)*3	Thiokol hardening agent
	Barium peroxide	-	Bleaching agent, explosives
Nitrates	Ammonium nitrate	102,188*1	Fertilizer, material for explosives, insecticide
	Sodium nitrate	22,735*1	Fertilizer, pharmaceuticals
	Potassium nitrate	5,736*2	Gun powder, fertilizer, catalyst
	Silver nitrate	(1,800)*2	Emulsion, medicine, catalyst
	Cadmium nitrate	(1,200)*2	Coloring agent, battery
	Nickel nitrate	(1,500)*2	Metal surface treatment, plating
	Cobalt nitrate	(350)*2	Petrochemical catalyst
	Barium nitrate	(1,366)*2	pyrotechnical products, optical glass, fireworks
	Ferric nitrate	(300)*2	Mordant, pigment, medicines
	Aluminum nitrate	(200)*2	Catalyst, mordant
	Zinc nitrate	(50)*2	Medicine, mordant, catalyst
	Lead nitrate	-	Reagent, match, antiseptics
	Magnesium nitrate	-	Pyrotechnical products, medicine material, catalyst
	Strontium nitrate	-	Fluorescent substance, fireworks, optical glass
	Thorium nitrate	-	Gas mantle, tungsten filament
	Calcium nitrate	-	Water soluble fertilizer, coloring
	Copper nitrate	-	Insecticide, catalyst, reagent
Permanganates	Potassium permanganate	794*2	Bleaching agent, removing agent

Note 1 Figure in ( ) is estimated.
Note 2 – denotes production unknown.
Note 3 *1: according to "Chemical Industry Annual Statistics", MITI (1984)
*2: according to "Chemical Products – 9586", Kagaku Kogyo Nippo (1985)
*3: according to survey by Japan Chemical Association

4.1.2 Hazard of fire and explosion by independent oxidizers

Accidental explosions due to impact or combustion of ammonium perchlorate [3,6] and accidental explosions of ammonium nitrate [1] and sodium chlorate [5,7,10] involved in fire are known. In addition to these substances, ammonium chromate, hydrazine nitrate and hydrazine perchlorate are listed in the Explosives Control Law of West Germany. Ammonium chlorate, ammonium nitrite, ammonium permanganate, chlorine dioxide, ozone, manganese dioxide, and others are known as unstable explosive oxidizers.

Ammonium perchlorate and ammonium nitrate [4] propagate detonation, while no test data on other explosive oxidizers according to standard test methods are available. Although many accidents of explosions involving chlorates in fire are known, no explosion of chlorates has taken place independently by the standard test methods [10]

Article 3.7.4 of this book shows the impact sensitivity of ammonium perchlorate and ammonium nitrate by the variable initiator test using a MKIII trajectory mortar; ammonium perchlorate is medium in sensitivity while ammonium nitrate is insensitive. In the case of ammonium perchlorate, the smaller the grain size, the higher the sensitivity. In the case of ammonia nitrate, powder is less sensitive than prills. Both ammonium perchlorate and prilled ammonium nitrate can produce explosive power equivalent to that of TNT (net swing of mortar about 150 mm). It should be noted, however, that the inner plastic cylinder used for the variable initiator test may participate in the reaction as combustible material.

Table 4.4 Oxidizers Exothermically Decomposing by DTA under Normal Pressure

Oxidizers	Temperature	Oxidizers	Temperature
Ammonium nitrate*	300℃	Ammonium perchlorate	300℃
Strontium nitrate	563℃	Potassium iodate	645℃
Mercurous nitrate monohydrate	750℃	Ammonium bichromate	250℃
Potassium chlorate	615℃	Ammonium dichromate dihydrate	250℃
Sodium chlorate	490℃	Potassium persulfate	285℃
Sodium chlorite	170℃		
Magnesium perchlorate Hexahydrate	375℃		

Temperature at which exothermic reaction starts.

* Exothermic reaction by closed cell DSC or pressurized DSC; only endothermic reaction under normal pressure.

Oxidizers were individually tested by DTA for their exothermic reactions. Table 4.4 lists oxidizers which showed an exothermic peak by DTA under normal pressure (temperature rise of 20 ℃ /min) [11] .In this table the temperatures at which the onset of exothermic decomposition occurs are indicated.

4.1.3 Contact ignition

Contact ignition is important because it may cause fire in an earthquake. Fires in five earthquakes since the Great Kanto Earthquake of 1923 have been recorded. These fires include some cases of contact ignition of oxidizers [1, 3] (2.5.1 of this book.).
Contact ignition occurs between two or more chemicals. Since there are numerous combinations of chemicals, it takes enormous time to carry out an effective experiment. The authors selected ethylene glycol to represent liquid organic substances, and thick sulfuric acid to represent acids, then examined contact ignition of oxidizers [1, 14] .
Table 4.5 lists oxidizers which ignited upon contact at normal temperature. Some oxidizers ignite upon contact with acids. Table 4.6 shows instances of exothermic reaction when sulfuric acid was added to a mixture of oxidizer and ethylene glycol. Oxidizer and acid should not be placed together because they generate toxic and pungent gases when they are mixed. It was also confirmed that potassium superoxide ignites when it contacts ethylene glycol.
Sodium chlorite in contact with sulfuric acid does not generate heat if the quantity is small. However, it can ignite from accumulated heat if the quantity is large. Table 4.7 shows contact reactions of oxidizers with combustibles other than ethylene glycol.

Table 4.5 Instances of Contact Ignition between Oxidizers and Ethylene Glycol at Normal Temperature by Improved Steel Dish Test(1)

Oxidizers	Time from contact to ignition
Sodium peroxide	90 sec
Chromium trioxide	0 sec
Potassium permanganate	10 sec
Bleaching powder	-*

* Only heat generation when contact between 2.5 g of each.
Ignition in 29 sec after contact between 500 g of each.

Table 4.6 Instances of Contact Ignition/Smoking between Mixtures of Oxidizer, Ethylene Glycol and Sulfuric Acid, According to Improved Steel Dish Test(3)

Oxidizers	Observasion	Oxidizers	Observation
Cesium nitrate	Smoke	Sodium bromate	Smoke
Strontium nitrate	Smoke	Potassium bromate	Smoke
Sodium nitrite	Smoke	Sodium iodate	Smoke
Bleaching powder	Ignition	Sodium chromate	Smoke
Sodium chlorite	Ignition	Potassium chromate	Smoke
Sodium chlorate	Ignition	Ammonium dichromate	Smoke
Potassium chlorate	Ignition	Sodium dichromate	Smoke
Barium chlorate	Ignition	Potassium dichromate	Smoke
Silver chlorate	Ignition	Barium peroxide	Smoke to ignition
Potassium perchlorate	Smoke		

Table 4.7 Results of Improved Iron Dish Test on Various Oxidizers and Combustibles*

Oxidizers	Sulfur		Red phosphorus		Sodium thiosulfate		Acetic acid		Ammonium chloride		Activated carbon	
	I	II	I	II	I	II	I	II	I	II	I	II
Bleaching powder (effective Cl>30%)	-	-		-		Rc				-		
Sodium chloride	Ig		Ig		Rc	Rc	Rc	Rc	-	-	-	-
Sodium chlorate	-	-		Ig	-	-	-	-		-		-
Silver chlorate	-	Ex	-	Ig		Rc	-					
Sodium nitrite	-	-		-	-	-			-	-		
Sodium nitrate	-	-		-		-						
Ammonium nitrate	-	-		-		-						
Mercury (II)nitrate	-	-		Ig		Rc						
Uranyl nitrate	-	-	-	Ig		Rc				Rc		
Potassium dichromate	-	-		-		-						
Potassium permanganate	-	-		-		-						
Chromium trioxide	-	-		-		-				-		
Sodium peroxide	-	Ig	Ig									

I = contact at normal temperature, II = contact at 100*C
Rc = reaction, Ig = ignition, Ex = explosion

Table 4.8 Results of Small Dewar Vessel Test on Oxidizers alone and Mixtures of Oxidizers and Ethylene Glycol, and Thermal Analysis

	Small Dewar vessel contact heat generation test			Thermal analysis of oxidizer					
				Mixture		Independent reaction start temperature (*C)			
Oxidizers	Temp. reached (*C)	Time (sec)	Heat generation	Heat gen. start temp. (*C)	Reaction heat (cal/g)	Dehydration	Fusion	Enthotherm. decomposition	Exotherm decomposition
Ammonium nitrate	100	900	No	253	610			230	
Aluminum nitrate $\cdot 9H_2O$	118	50	Yes (large)			60-			
Lithium nitrate				318	201		270	600	
Sodium nitrate	100	300	No	205	130				
Potassium nitrate	100	300	No						
Cesium nitrate	100	300	No e)						
Magnesium nitrate $\cdot 6H_2O$	111	0	No b)	210	249	95-			
Calcium nitrate $\cdot 4H_2O$	100	300	No	175		60			
Strontium nitrate	100	300	No	276					563
Barium nitrate	100	300	No	300	28			600	
Chrome nitrate			e)	146	320				
Cobalt nitrate $\cdot 6H_2O$	100	300	No e)	160	313	55-			
Nickel nitrate $\cdot 6H_2O$	100	300	No e)	164	286	53-			
Cadmium nitrate $\cdot 4H_2O$	100	300	No						
Zinc nitrate $\cdot 6H_2O$	100	300	No e)	150	225	45-			
Silver nitrate	100	900	No a) e)	180	317		210	457-	
Ferrous nitrate $\cdot 9H_2O$	118	0	No b)			45-			
Cupric nitrate	125	300	Yes	152	156	90	132	165-	

· $3H_2O$			(small)[e]						
Mercurous nitrate	144	36	Yes	120	93	45			750-
· $1H_2O$			(large)						
Lead nitrate	100	300	No [e]	196	317			420	
· $6H_2O$									
Sodium nitrite				277	371				
Silver nitrite	100	300	No [e]	185	282				
Sodium chlorate			[e]	207	746				
Potassium chlorate	100	300	No [e]	197	550			470	615
Barium chlorate			[e]	175	260	80	465	400-	
· $1H_2O$									
Silver chlorate	107	600	Yes	155	790				
			(small)						
Sodium chlorite	>600	13	Yes	100	708				
			(large)[a] [d]						
Sodium perchlorate	100	300	No	258	408			265-	
Potassium perchlorate	100	300	No [e]	230	246				
Magnesium perchlorate	117	0	No [b]	254	1075	105			375
· $6H_2O$									
Ammonium perchlorate	100	300	No [e]	227	649		262		300
Cobalt perchlorate	255	466	45		210-				
· $6H_2O$									
Lithium perchlorate	110	0	No [b]	271	242			258-	
· $1H_2O$									
Ferrous perchlorate	100	300	No			60		250	
· $6H_2O$									
Sodium bromate				145	687				
Potassium bromate	100	300	No	158	598			370-	
Sodium iodate	100	300	No	200	297			545-	
Potassium iodate				200	216			518	645
Barium iodate	100	300	No	222	203	60	420	615-	
· $1H_2O$									
Iodic acid	180	68	Yes	112	186		135	353	
			(large)						
Silver iodate	100	300	No	258	139		390	435-	
Sodium chromate	100	300	No	208	8				
· $4H_2O$									

Silver chromate	107	420	Yes (small)	108	202		490	675-	
Ammonium bichromate	244	21	Yes (large)	121	250				165
Sodium bichromate · $2H_2O$	167	55	Yes (large)	125	228				250
Potassium bichromate	185	460	Yes (large)	146	98				
Silver bichromate	100	300	No						
Potassium permanganate	(Ignition at normal temperature)								
Sodium peroxide	(Ignition at normal temperature)								
Barium peroxide	100	480	No	143	226				
Trilead tetroxide	100	300	No						
Chromium trioxide	(Ignition at normal temperature)								
Potassium persulfate	138	90	Yes (large)	128	313				285

a) Silver separation was observed.

b) 11 °C at the moment of mixing. Temperature rose, but no heat was generated thereafter.

c) Oxidizing agent of 0.5 g was used to avoid explosion.

d) Weak explosion was heard.

e) Heat was generated when 140 °C small Dewar vessel test was performed.

4.1.4 Hazard of thermal explosion and stability of substances composing oxidizers

In order to determine the stability of mixtures of oxidizers and combustibles, the SC-DSC (temperature rise of 10 °C/min) of mixtures of oxidizers and ethylene glycol was measured[11]. The results are shown in Table 4.8. It should be noted that the stability of a mixture of oxidizer and ethylene glycol cannot be assumed from the reactivity of the oxidizer itself.

Since a very small quantity of specimen is used for DSC or DTA, the heat of reaction is not accumulated in the system. However, heat is accumulated when a composite of oxidizer and combustible ignites spontaneously. Therefore there is a question of whether the stability of a composite can be determined only by micro thermal analysis. In view of this question, a small Dewar vessel, which is safe and heat-retaining, was used for this test 11, 12) ; part of the results are shown in Table 4.8 (results of 100 °C small Dewar vessel). The Dewar vessel test was also carried out at 140 °C , and the oxidizers which generated heat in this test are indicated with e) in the Table.

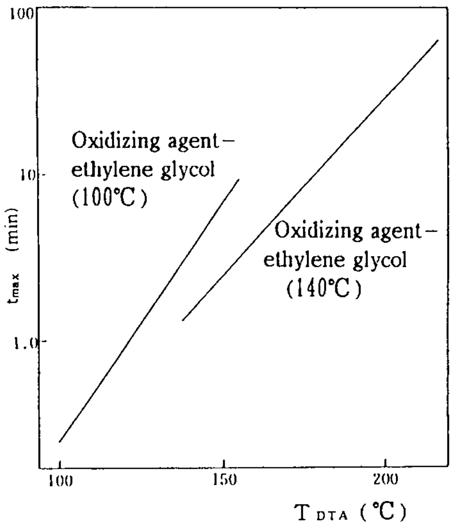

Fig. 4. 1 Mixture of oxidizer and ethylene glycol (1:1) was tested in a small Dewar vessel at 100°C and 140°C. The logarithms of the time to reach maximum temperature (t_{max}) againsy the temperature at the onset of decomposition (T_{DTA}) are plotted.

Fig.4.1 shows the relationship between the maximum temperature reached in the small Dewar vessel test and the temperature at the start of heat generation in DTA. Although the DTA decomposition starting temperature of a mixture of ammonium perchlorate and diethylene glycol is 230 °C , this mixture showed self-accelerated exothermic reaction in 64 minutes in the 140 °C small Dewar vessel test. It should be noted that reaction temperatures depend significantly on heat accumulation.

If the quantity of mixture is small, a DTA reaction may not be observed. For instance, Fig. 4.2 shows DTA curves for a mixture of potassium chlorate and diethylene glycol. When the sample weighs 1.6 mg, almost no heat generation is observed (the lower curve). When the sample weight increases to 3.1 mg, an exothermic peak is clearly observed. Since almostno heat is accumulated in the sample in case of DTA, one component of mixture may react while the other

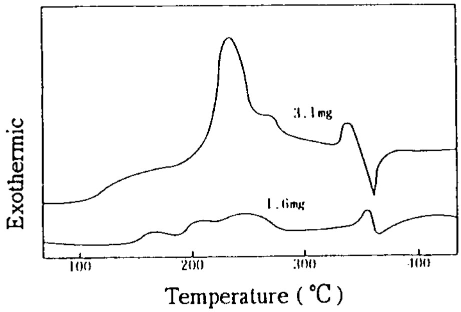

Fig. 4. 2 SC-DTA Curves of $KClO_3$ -$(HOCH_2CH_2)_2O$

component does not. When the quantity of the mixture is larger, the product of the reaction of one component may catalytically promote the reaction of the two components.

The reactivity of an oxidizer varies depending on the combustible substance used. Sulfur and red phosphorus are higher in reactivity with sodium chlorite and sodium chlorate than ethylene glycol.

4.1.5 Combustion hazard of oxidizer compositions

Up to now, the common assessment method of the hazards of solid oxidizers is merely burning rate tests of mixtures of oxidizers and wood powder or cellulose. For the burning rate tests of combustible solid particles, the following methods are used: the IMO method (proposed by UK), the Rutubo method, the TNO methed, the US method, the US Transport Ministry method, the US Bureau of Mines method, the UK time/pressure test, and the modified time/pressure test. We have studied the IMO method, the TNO method and the modified time/pressure test. Burn hazards were described in the first book 1) and in Section 3.5 of this book.

4.1.6 Explosion hazards of oxidizer mixtures

Hazards of detonation and violent combustion of oxidizer mixtures are generally evaluated by tests of detonation–propagation, initiation sensitivity and explosion power. For oxidizer mixtures explosiveness is important. To ensure the safety of operaters, it is necessary to investigate the mixing ignition, stability and super high–sensitivity with a small mass of sample before the practical test. In this field Treumann has done much of the work 1, 15) .

(1) Initiation sensitivity of oxidizer mixtures

In oxidizer mixtures, the range of initiation sensitivity is very wide from super high sensitivity to very low sensitivity. Test methods differs with sensitivity. For super high sensitivity mixtures, testing must be carried out with only a small mass of sample because of their explosiveness. On the other hand, the determination of explosion is readly made. The small drop ball test(Sec. 3.3) is reasonable.

For mixtures with median sensitivity, it is difficult to determine whether explosion happens or not in the drop hammer test. Variable initiator tests using the ballistic mortar(Sec. 3.3) are better.

For mixtures with low sensitivity, detonation–propagation must be investigated. For example, we cannot say the mixture possesses hazards of explosion if it cannot sustain propagation of detonation. A large quantity of sample is necessary in tests of this kind. Because of the noise of explosion, the explosion test under sand (Sec.3.8)is recommeded.

Most of mixtures of oxidizer and red phosphorus possess very high sensitivity. The results of drop hammer tests for this kind of mixture is shown in Sec.3.3. In the range of experiments, the mixtures of red phosphorus with bromite, chlorite and sodium peroxide possess very high sensitivity.

The order of initiation sensitivity of mixtures of oxidizer and combustible is difficult to determine in oxidizers or in combustibles alone. Chlorite and bromite tend to possess very high sensitivity, but, for different combination of cations the order of sensitivity is different.

When charcoal is taken as a combustible, the experimental results of determining sensitivity in small gap test and the variable initiator test are shown in Sec.3.7. The order of sensitivity of the mixtures of oxidizers with charcoal and red phosphorus is as follows:

For charcoal: $NH_4ClO_4 > KClO_3 > KClO_4 > KNO_3 > Ba(NO_3)_2$

For red phosphorus: $KClO_3 > NH_4ClO_4 > KClO_4 > KNO_3 > Ba(NO_3)_2$

For potassium nitrate as the oxidizer, the order of sensitivity of combustibles is:

Al > S > Ti > charcoal

The sensitivity of composite propellant is lower than predicted from the mixture of NH_4ClO_4−Al.That may be because the composite propellant is a solid rather than a powder.

4.1.7 Practical test methods suited to solid oxidizers

The following two test methods are suited to solid oxidizers according to the classification of Fire Service Law.

1−Drop ball test (Sec.3.3.7)

2−Burn test (Sec.3.5.2)

Criteria for test results are described below. Firstly, drop ball test will be stated.

1 (6) Criteria for the drop ball test

When tested samples are mixed with combustibles, their grade of explosion hazards corresponding to every case of (5)2 is (Sec.3.3.7):

Case A	Rank I
Case B	If the number of explosions is more than 20, rank I; otherwise, rank II
Case C	Rank II
Case D	Rank III
Case E	If the number of explosion is more than 20, rank II; otherwise, rank III

2 (6) Criteria for the burn test

The potential oxidizing hazards of tested samples are divided into the following grades(Sec.3.5.2):

When the burning time of a tested mixture is shorter than that of potassium bromite, it is in rank I. When the time is longer than that of potassium bromite and shorter than that of potassium perchlorate, it is in rank II. When the time is longer than that of potassium perchlorate, it is in rank III.

3−Total criteria

By combining 1(6) with 2(6), dangerous substances can be determined from Table 4.9. I represents high oxidizing hazard, II represents medium and III low oxidizing hazard. IV represents no hazard.

Table 4.9 Total criteria of solid oxidizers

Burn test drop ball test	Rank I	Rank II	Rank III
Rank I	I	I	I
Rank II	I	II	III
Rank III	I	III	IV

Next, two test methods suited to formed products of solid oxidizers will be described.

1−500 g burn test(Sec.3.5.4)

2−50/60 steel tube test(3.8.3)

1 (6)Criteria for the 500g burn test:

If the burning time of a sample is shorter than that of a standard sustance, the tested sample is hazardous.

2 (6)Criteria for the 50/60 steel tube test:

If detonation is complete, the tested sample is hazardous.

3 Total criteria

If the sample satisfies 1(6) or 2(6), it belongs to the class of dangerous substances, and the grade is shown in Table 4.10.

Table 4.10 Total criteria of formed products of solid oxidizers

Steel tube test Burn test	Danger	No danger
Danger	※	III
No danger	III	No

The meaning of III is same as that in Table 4.9. The symbol ※ implies that the hazard grade must be established by test results on a powdered sample of the formed products.

In addition, the following tests are recommended for use with solid oxidizers, but it is not necessary to do every test.

a. Explosiveness and stability of oxidizers themselves

a.1 SC−DSC test (Sec.3.2)

a.2 Variable initiator test (Sec.3.7.2)

a.3 50/60 steel tube test under sand (Sec.3.8.2)
b. For mixtures of oxidizer and combustible
a.1 SC−DSC test (Sec.3.2)
b.2 Ignition test (Sec.3.4.2)
b.3 Drop ball test (Sec.3.3.1)
b.4 BAM friction sensitivity test (JIS K 4810−1979)
b.5 Small gap test (Sec.3.7.3)
b.6 Variable initiator test (Sec.3.7.2)
b.7 Burn test (Sec.3.5.2, p.121 in book [16])
b.8 50/60 steel tube test under sand (Sec.3.8.2)

4.2 Combustible Solids

4.2.1 Test methods in the Fire Services Law

For combustible solids defined in the Fire Services Law, the small gas flame test(Sec.3.4.2) is used.

4.2.2 Other methods

For self−propagation, the IMO burning rate test(p.121 in book [16]) is suitable. In addition, the dust explosion test (p.223 in book [16]) is recommended when combustible dusts are evaluated.

4.3 Spontaneously Ignitable Substances and Water−Reactive Substances

4.3.1 Test methods for spontaneously ignitable sustances based on the Fire Services Law(U)

1−spontaneous ignition test
(1) The purpose of test
The purpose of this test is to investigate the hazards of solids or liquids in air. A sample is retained in air for a given time to observe if it ignites spontaneously.
(2) Samples
The tested samples must be powders or in small pieces [*1] .
If the tested samples are stored in containers, after opening they must be quickly used in the tests. If a solid sample is stored in a protective solution, the solution must be separated from the sample by use of filter paper [*2] and tested as quickly as possible.
(3) Test conditions

Test conditions of temperature 20 ± 5 ℃ , humidity 50 ± 10%, atmospheric pressure and no wind are suitable [*3] .

(4) Test procedure

A For solid samples

a. 0.5 ~ 1cm^3 of sample is placed on the center of a dry filter paper [*5] 9 cm in diameter on a china cup [*4] to observe whether it ignites spontaneously in 10 minutes. If it does not ignite spontaneously, the above process is repeated 5 times.

b. If a powdered sample does not ignite spontaneously in test a, 1 ~ 2cm^3 of sample is dropped on an inorganic adiabatic plate [*6] 1 m × 1 m from a height of 1 m to observe whether it ignites spontaneously in the process of falling or within 10 minutes. If it does not ignite spontaneously, the above process is repeated 5 times.

B. For liquid samples

a. 0.5 ~ 1cm^3 of sample is dropped within 30 seconds into a 7 cm diameter china cup from the height of 1 ~ 2 cm by use of a injector or pipe to observe if it ignites spontaneously in 10 minutes. If it does not ignite spontaneously, the above operation is repeated 5 times. In the case of no spontaneous ignition, it is necessary to observe whether gas evolution occurs. Evolved gas is placed at the side of a small flame to observe whether it ignites to determine if the gas is combustible gas.

b. In the case of no spontaneous ignition but occurence of combustible gas, 0.5cm^3 of sample is dropped within 30 seconds on a dry filter paper, 9 cm in diameter, on a china cup 7 cm diameter, from the height of 1 ~ 2 cm, to observe whether it ignites spontaneously, or the filter paper is burnt in 10 minutes [*7] . If it does not ignite spontaneously or the filter paper does not burn, the above process is repeated 5 times.

(5) Criteria

a. A solid material will be classfied as a dangerous good if it ignites spontaneously at least once in test (4)a.

b. A liquid material will be classfied a dangerous good if it ignites spontaneously or the filter paper is burnt at least once in test (4)b.

4.3.2 Spontaneously ignitable materials in Bretherick's book

Spontaneously ignitable materials 18) in Bretherick's book 17) are listed in Table 4.13. However, spontaneously ignitable materials defined here contain not only those which ignite spontaneously in contact with air at room temperature as defined in the Fire Service Law but also those which ignite spontaneously when stored in air for a long time.

4.3.3 Test methods for water-reactive materials in the Fire Services Law(V)

2-Reactive test with water

(1) The purpose of the test

The purpose of the test is to determine the hazards of ignition and of the formation of combustible gas from solid or liquid materials when they contact water.

(2) Samples

If the test samples are stored in containers, after opening they must be quickly used in tests. If a solid sample is stored in a protective solution, the solution must be separated from the sample by use of filter paper *2 and the sample tested as quickly as possible.

(3) Test site

Same as 1(3)

(4) Test procedure

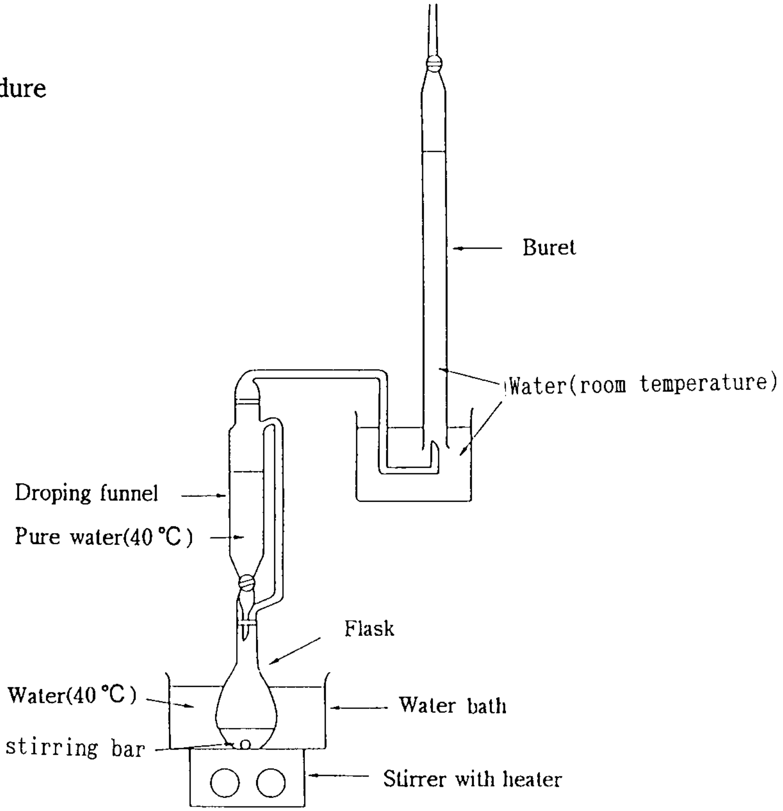

Fig. 4.3 Experimental equipmental for reactivity with water

The test is as follows:

A(a) A filter paper support *8 is placed in the bottom of a 500 ml beaker. Pure water (ion exchanged water or distilled water) is added to the beaker up to the surface of the support. A piece of filter paper, 7 cm in diameter, is laid on the support, just touching the water so that the filter paper can be lifted. A small amount of sample (solid: greater than 2mm diameter, liquid: 4mm ^{3}) is laid on the center of the filter paper to observe whether any evolved gas ignites spontaneously. If gas ignites spontaneously, the above operation is repeated 5 times.

If there is no spontaneous ignition, the evolved gas is directed at the side of small flame to observe if it ignites to determine whether the gas is combustible.

In the case of spontaneous ignition, the following test must be conducted.

(b) In the case of no spontaneous ignition but evolution of a gas (or if evolution of a gas is uncertain) in test (a), the quantity of sample must be increased(solid: 2 times diameter of test (a), liquid: 50 mm^3); the same test as (a) is conducted to observe whether gas occurs or ignites spontaneously. If the gas ignites spontaneouly, the above operation is repeated 5 times.

In the case of no spontaneous ignition, the evolved gas is directed at the side of a small flame to observe if it ignites to determine if the gas is combustible or not. However, in the case of a definite answer in test (a), this step is unnecessary.

B In the case of no spontaneous ignition of gas or uncertainty about the combustible nature of the gas or the occurence of gas, a large sample (maximum 2 g) is put into a flask of 100 ml volume to obtain 100 ml of gas. The flask is put into a water bath at 40 ℃. Pure water (ion exchanged water or distilled water) at 40 ℃ is rapidly dropped into the flask from a dropping funnel. The sample is agitated [*9].

The quantity of gas inside the flask is measured every hour for 5 hours [*10]. The maximum gas generation in any 1 hour (~ m^3/(kg · hour))is taken as the maximum gas generation. The same operation is repeated 5 times; the maximum value observed is used.

(5) Criteria

If the generated gas ignites in test 4(a), or the generated gas burns when it is directed at the side of small flame, or the maximum gas generation is greater than 0.2m^3/(kg · hr), the sample is classified as a dangerous good.

4.3.4 Materials that react with water in Bretherick's book

Materials [18] that react with water in Bretherick's book [17] are listed in Table 4.14. However, materials recorded here contain not only those which generate combustible gas in contact with water at room temperature as defined in the Fire Service Law but also those which generate heat or poisonous gas when they contact water, and also those which react only with water at high temperatures.

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Chapter 5

SAFETY ASSESSMENT OF PYROTECHNICS

5.1 Introduction

Pyrotechnics include reactive chemicals. The technology of hazard assessment of reactive chemicals can be applied to pyrotechnics to increase safety. The safer pyrotechnic products are the better.

Hazard assessment of reactive chemicals is very important in making correct regulations and preventing accidents, but it is not used by many people dealing with pyrotechnics. This may be because they are very busy with The development of new products. However, as a safe pyrotechnics technology is of direct benefit to persons who want to develop new pyrotechnics, hazard assessment deserres be paid great attention.

In this chapter, examples of hazard assessment of pyrotechnics will be described.

5.2 Safe Package of Sporting Paper Caps

5.2.1 Introduction

The sporting paper caps which are used for starting signal pistols in Japan each contain about 0.05 g of a composition consisting of 74% potossium chlorate, 18% red phosphorus, 8% sulphur and small amount of starch. Recently, the hazard classification on the packaging of these paper caps for transportation on ships was discussed.

The sporting paper caps are used in athletic contests, games and sports in every country, and transported world wide, sometimes by sea. With conventional packaging of the paper caps, an explosion occuring in the package may propagate through all the contents and damage the surroundings.

First, sheet corrugated board was shown to perform well in absorbing shock in tests in which three sheets of corrugated board were put into a small case and the cases used as shock absorbers for preventing the propagation of explosion from a detonator. Second, the safety of the new package was shown by applying the United Nations classification tests for explosives.

The commercial products of RADIE Co. Ltd. (trade name EVERNEW) were used as the sampls of sporting paper caps. Fig.5.1 and Fig.5.2 show the structures, cases and packages of the sporting paper caps.

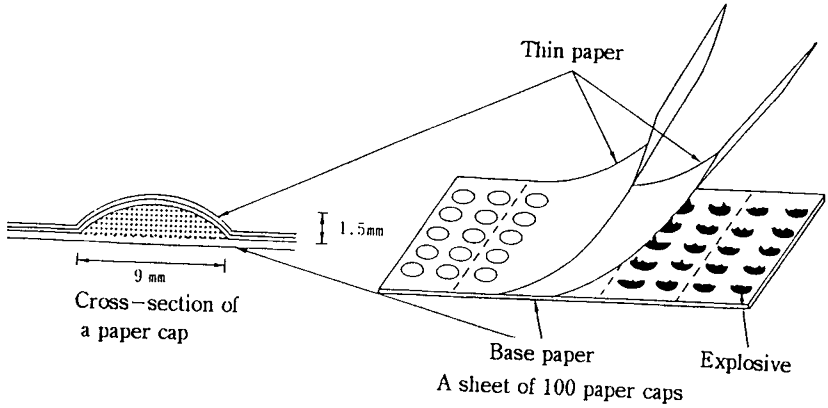
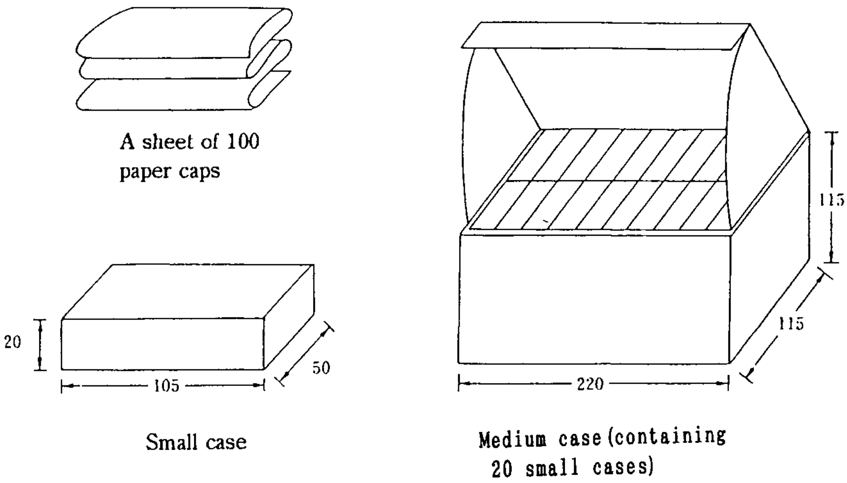


Fig. 5.1 Cross-section and sheet structure of sporting paper cape



A sheet of 100
paper caps

Small case

Medium case (containing
20 small cases)

Fig. 5.2 Sheet and case of sporting paper caps

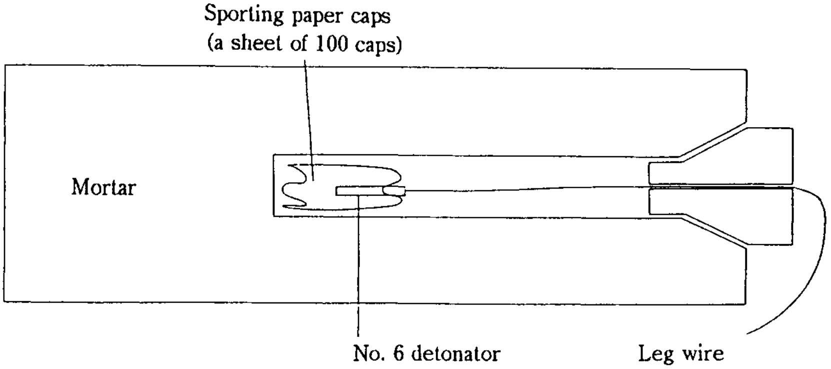


Fig. 5.3 MKIII ballistic mortar into which a sheet of paper cap was inserted

5.2.2 Explosive power

The explosive power of 100 sporting paper caps (about 5 g of explosive)was measured by use of MKIII ballistic mortar initiated by a No.6 detonator as shown in Fig.5.3.
The length of the ballistic pendulum swing from the explosion of 100 sporting paper caps and one No. 6 detonator is 165 mm. That from only one No.6 detonator is 30 mm, so the net result from 100 sporting paper caps is 135 mm. In comparison with a 151 mm swing from 5 g of TNT, the explosion power of the sporting paper caps is 89% of that of TNT.

5.2.3 Impact and shock sensitivity

(1) Impact sensitivity
Impact sensitivity in the direct drop ball test is $\log E_{50} = -1.34$, $\alpha = 0.04$. The variation is small.
(2) Shock sensitivity in the small gap test by use of the MKIII ballistic mortar
ten sporting paper caps(about 0.5 g of explosive) which are formed into circle of 10 mm diameter are put into a glass tube with a 12.4 mm inner diameter as shown in Fig.5.4. Shock absorbing material is laid on the caps, ane a No.0 detonator is inserted. The test tube is put into a MKIII ballistic mortar, a 2 kg projectile is installed,and the No.0 detonator is initiated.
The test results are shown in Table 5.1. B' is the relative power to TNT. Even if the length of gap is increased up to 110 mm, the paper caps explode, so we cannot determine the length of gap in which the paper caps do not explode. It is known that for some substances with $\log E_{50} = -1.34$ in drop ball test, they cannot be measured in the small gap test.

Table 5.1 The test results of sporting paper caps in small gap test by use of MKIII ballistic mortar

Length of gap(mm)	Length of pendulum(mm)	B'(TNT equivalency%)
40	12	80
60	10	67
80	11	73
110	12	80

(3) Small gap test(not using the ballistic mortar) (II)
In a shock sensitivity test using a polyethylene sheet as a shock absorbing material,

many pieces of the polyethylene sheet must be used to determine the point at which paper caps do not explode because of their highsensitivity. The test tube cannot be put into the ballistic mortar.

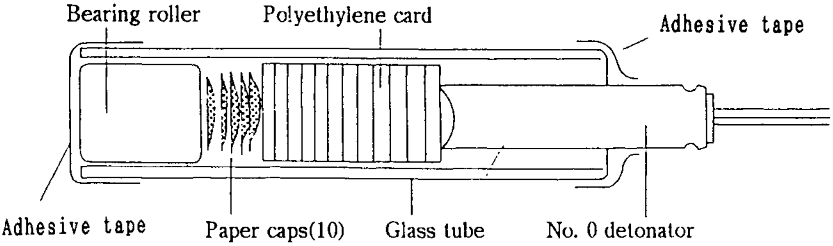


Fig. 5.4 Set−up for gap test using MKIII ballistic mortar and paper caps

The test sample is initiated, then observed for changes in the paper caps to determine whether an explosion has occurred. A glass tube or rolled paper tube is used as a vessel; the test sample is shown in Fig.5.5. Five paper caps were each cut in a circle and laid one on topot another. The shock absorbers were cut into cireles, and powderery absorbers were poured into the tube and their length measured. Because shock absorbing by polyethylene sheets and a steel roller is not very effective, to prevent damage by the jet from the detonator, a steel roller and a polyethylene card were placed on the absorber. The thickness of polyethylene is 8mm. A detonating shock was given by a No.0 detonator which was placed on the polyethylene card.

The shock absorbing materials used, their abbreviations and their sizes are shown in Table 5.2.

Table 5.2 Abbreviations and sizes of shock absorbing materials

Materials	Abbreviation	Sizes(mm)
Double side corrugated board	C.B.III	Thickness 5
Double side corrugated board A/F	C.B.AF	Thickness 5
Double side corrugated board AB/F	C.B.AB	Thickness 6.5
Double side corrugated board AA/F	C.B.AA	Thickness 7
Polyethylene card	P.E.C.	Thickness 2
Bearing roller	B.R.	Thick.12, Dia.12
Glass microspheres	G.M.B.	
Ottawa sand	O.S.	
River sand	R.S.	
Talc powder	T.P.	

The results of small gap test (II) are shown in Table 5.3 and Fig.5.6. From these results it can be seen that propagation of the shock waves from the No.0 detonator differs with the kinds of propagation media used. The shock–absorbing effect changes in the following order: polyethylene card < steel < Ottawa sand < corrugated board < talc < glass microspheres. The data on Table 5.3 show that corrugated board is effective in absorbing the shock of the explosion of the detonator, but the effect is smaller when compressed board is used. As to the material of the test vessel, it made no difference whether glass or paper was used. These results indicate that corrugated board and river sand each possess good shock–absorbing properties, that it is not suitable to use polyethylene card as a gap in small gap test for substances possessing very high sensitivity, and that glass microspheres, Ottawa sand, and talc may be used as gap materials.

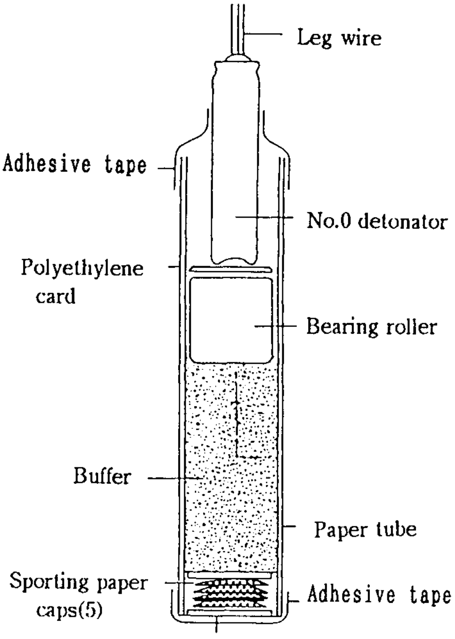


Fig. 5.5 set-up for small scale gap test (II)

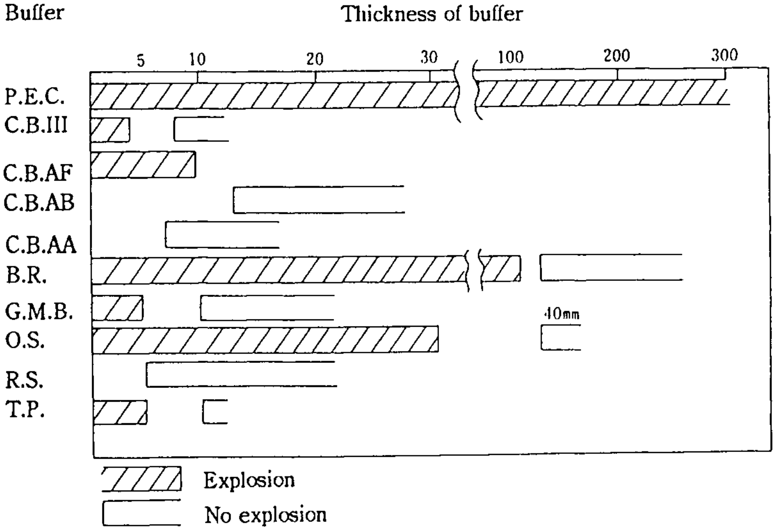


Fig. 5.6 Buffering effect of different materials

Table 5.3 The results of small gap test(II) of sporting paper caps

Shock absorbig materials	Tube materials	Length of gap (mm)	Results
Polyethylene card	Glass	150	○○○○○
		300	○○○○○
Double side corrugated board III	Glass	30*	×××××
Thickness 3mm (compressed)		15*	○○×××
Thickness 4mm(general)	Paper	12	×××××
+1P.E.C.+1B.R.		8	×××××
		4	○○○○○
Double side corrugated board AF S125		13*	○○○○○
Thichness 2.6mm(compressed)		26*	○○○○○
Thickness 5mm(general)		52*	×××××
+1P.E.C.+1B.R.		39*	×××××
		10	○○○○○
Double side corrugated board AB/F S125		26	×××××
Thickness 5.5mm(compressed)		13	×××××
Thickness 6.5mm(general)		11*	○○○○○
+1P.E.C.+1B.R.			
Double side corrugated board AA/F S160		14	×××××
Thickness 7mm		7	×××××
+1P.E.C.+1B.R.		5	○○○○○
Bearing roller 12mmϕ × 12mm thick		252	×××××
		132	×××××
		72	○○○○○
		96	○○○○○
		120	○○○○○
	Glass	132	×××××
Glass microsphere C15	Paper	20	×××××
+1P.E.C.+1B.R.		10	×××××
		5	○××××

Ottawa sand, 200～300 mesh +1P.E.C.+1B.R.	20	○○○○○
	30	○○○○×
	40	×××××
River sand +1P.E.C.+1B.R.	20	×××××
	10	×××××
	5	×××××
Talc powder +1P.E.C.+1B.R.	10	×××××
	5	○○○○○

* :Compressed corrugated board is used.
○ :Explosion × :No explosion

5.2.4 Tests of sympathetic propagation between small and medium cases of sporting paper caps

Three corrugated boards (40mm × 100mm × 5mm) were inserted between small cases containing 100 paper caps,and one case was initiated by a No.6 detonator to determine whether sympathetic explosion of the adjoining cases occured. Next, small cases containing three corrugated boards were interposed between small cases containing 100 signal caps placed one by one in a medium case. The medium case was initiated by a No.6 detonator from the outside and the situation was examined for sympathetic propagation.

The results are shown in Table 5.4. Paper caps in a small case could be initiated by a No.6 detonator. Sympathetic explosion occured when three corrugated boards were inserted into two small cases. However, when a small case containing three corrugated boards was inserted into two small cap cases, the paper caps did not explode but only partially burned. When the above set was placed into a medium case and initiated by a No.6 detonator, two cases exploded, 2 ～ 3 cases burned, and the rest neither exploded nor burned. The mixing of sporting paper caps with such strong initiaing sources as No.6 detonators is not permitted; if packages such as those in test 4 and test 5 are used, the explosion of the total package can be prevented.

5.2.5 Burning test for the medium case containing caps

The flame of a signal flare was applied to a outside of the medium case containg 20 small cases for five minutes, and the burning behavior was taken place. After 30 seconds partial burning but no explosion had occured.

Table 5.4 test results for the sympathetic explosionof sporting paper caps inside small cases

○ Explosion, △ Burning, × Neither explosion or burning,

☐ Small case in which 3 pieces of corrugated boads were inserted,

● No. 6 detonator

Test No.	Test seting and results										
1	●	○		○							
2	●	○		○		△					
3	●	○		○		△		△			
4	●	○		○		△		×		×	
			△		×		×		×		×
5	●	○		○		△		△			
			△								
6	●	○				×		×		×	
			×		×		×		×		×

5.2.6 The pressure vessel test

The UN pressure vessel test was applied to one sheet of sporting paper caps (about 5 g of explosive). The bursting pressure of the rupture disk was 5.9 kg/cm ^{2} , and the average rate of temperature rise was 30 ℃ /min.

The test results are shown in Table 5.5. Because the paper caps are well-sealed they decompose violently when heated.

Table 5.5 Results of pressure vessel test on sporting paper caps

Orifice (mm)	Rupture(○) or no rupture (×)
10	○
12	○ 1)
14	× 2) × 3) ○ 4)
16	× 3) ○
18	○
20	× 2) ○

1) Ejected caps burned outside the vessels
2) Flame was ejected from the nozzle
3) The rupture disk swelled
4) Unburned caps ejected

5.2.7 UN test methods

The UN classification of explosive packages consists of three kinds of tests: i.e. the single package test, the stack test and the external fire test.

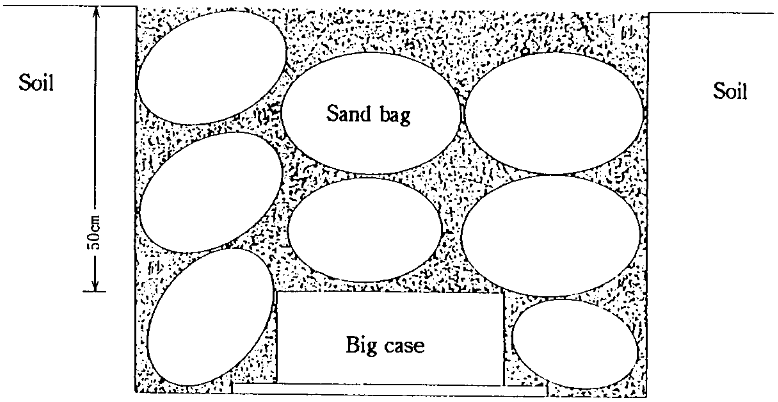


Fig. 5.7. Test installation for a single package

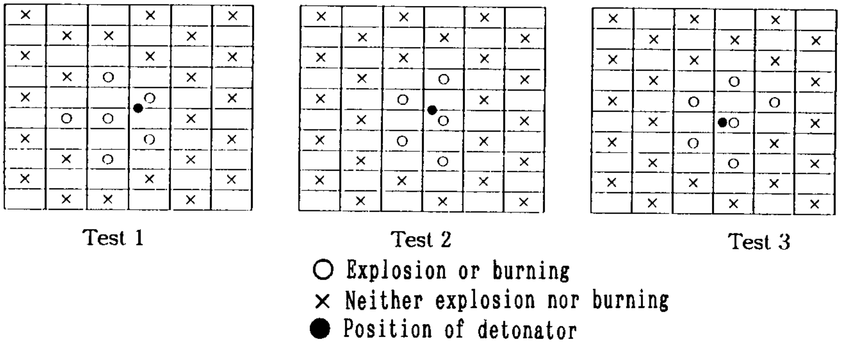


Fig. 5.8 Test results for a single package

5.2.8 The single package test

The single package test was applied to a large case containing the sporting paper caps. A round hole 80 cm in diameter, and 70 cm deep was made in the ground and the case was placed in the hole. Sand bags were placed on it and gaps between the case and sand bags were filled with river sand. Before placing the case in the hole, a No.0 detonator was inserted between two small cases which were situated in the center of the large case.

The results are shown in Fig.5.8. In three tests, only 5 or 6 small cases exploded or burned and others were left unchanged. The burning was not propagated to the surroundings.

5.2.9 The stack test

A package of five large cases containing sporting paper caps was placed in a hole in the ground,and the stack test was carried out similarily to the single package test.

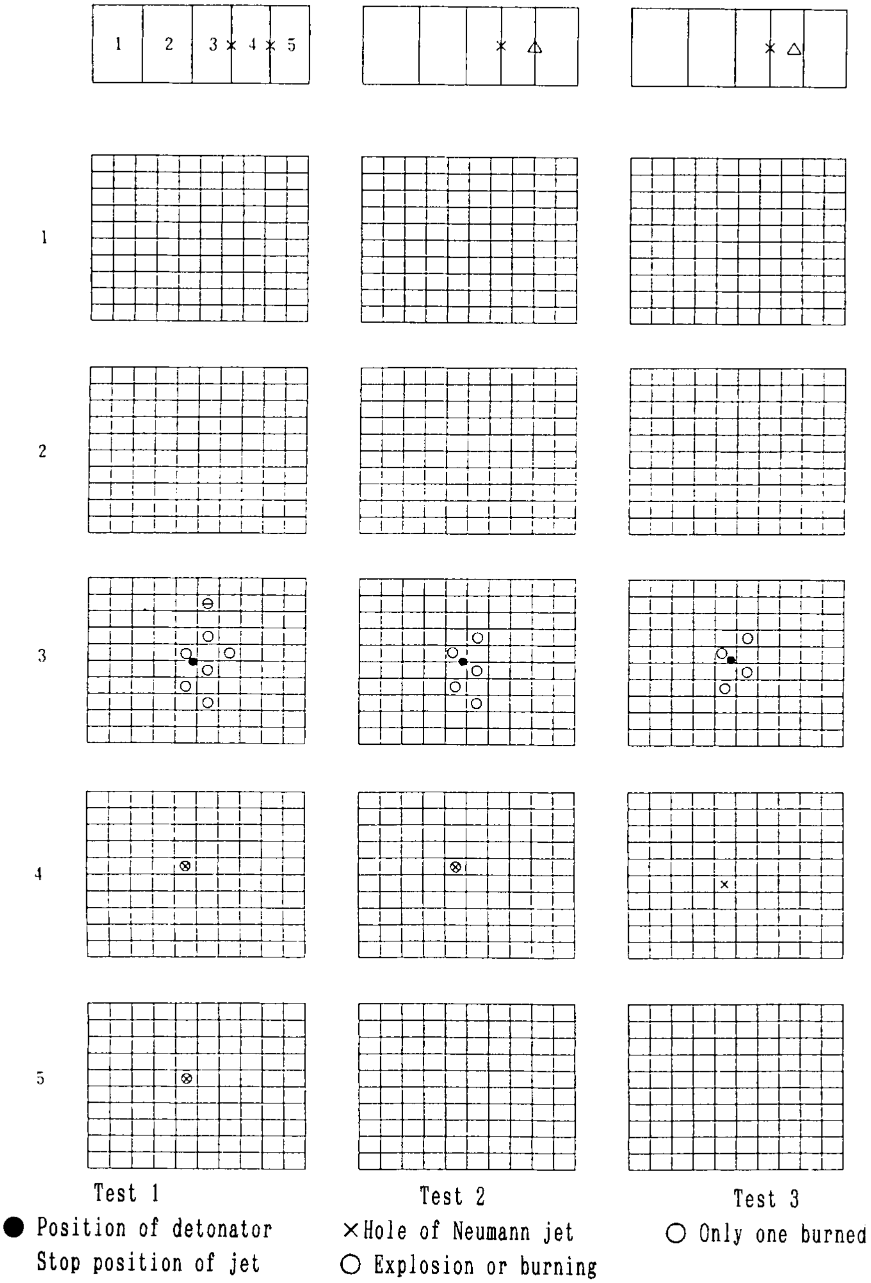


Fig. 5.9 Test results for a stack package

The results are shown in Fig.5.9. Except for the large case in which the detonator was inserted, other cases exploded because of the Neumann jet.The fragments of the detonator are, shown in Fig.5.10.

If there is no effect of the Neumann jet, the results are similar to those of the single package test; no propagation of explosion or burning was observed. The situations after the tests are shown in Fig.5.11 and Fig.5.12.

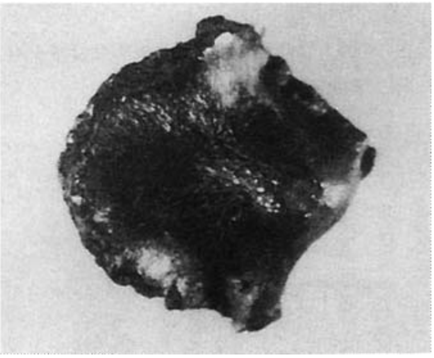


Fig. 5.10 Neumann jet of No. 0 detonator

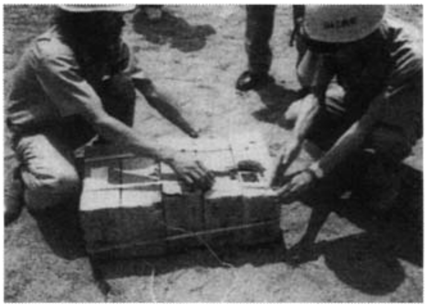


Fig. 5.11 Result for a stack package

5.2.10 The external fire test

(1) Purpose

The purposes of this test are to investigate the , damage to surroundings from shock waves, the effect of heat and fragments, from any explosion and the damage level for stack packages when they are heated by a fire.

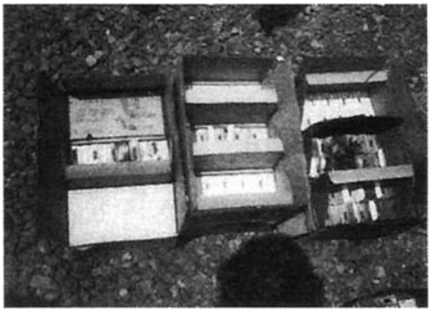


Fig. 5.12 Results of test 1 for a stack package
From left: Inside of No. 5, No. 4 and No. 3

(2) Suitable conditions

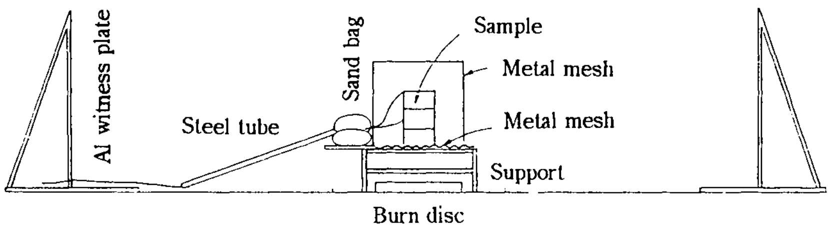
The test is suitavce for packages and unpacked stacks of explosives when they are transported. At least 3 cases are placed on a frame;a strong external fire is sustained for sufficrent fime to heat the explosives. The heating rate is similar to that expected in transportation accidents. It is unnecessary to conduct tests underexactly the same condition as the practical cases. As a fuel, wood, liquid fuel or a propane burner can be chosen. The best is wood.

(3) The installation

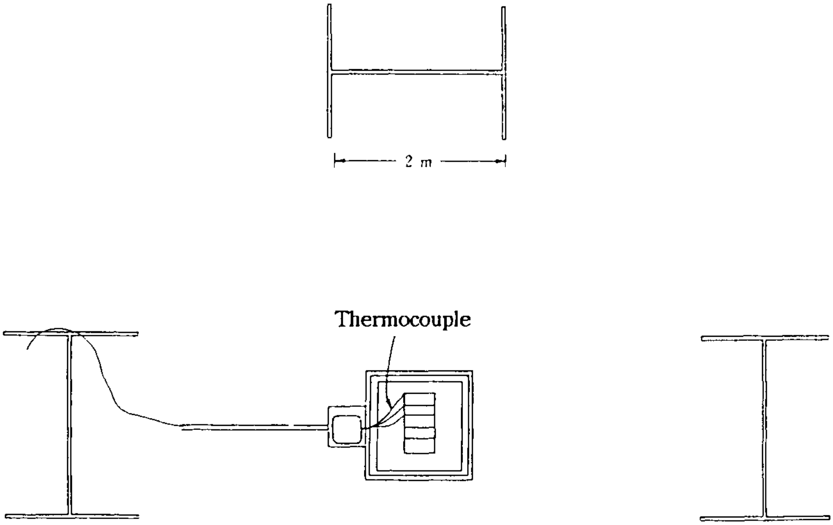
The installation is shown in Fig.5.13.

(4) The test procedure

(a)Preparing a test for a large case



Front view



Upper view

Fig. 5.13 Experimental installation for the external fire test

To observe the burning situation of sporting paper caps, one begins with a burning test one a larg case containing 3000 caps.

Ten liters of water(to avoid overheating), 10 liters of light oil and 1 liter of gasoline are poured into a container. A large case of caps is laid on the metal frame. Two nickel–chrom wire ignition balls are placed at two corners of the containers. After all people are moved 100 m away from the site, it is ignited. The phenomena were observed and recorded by eyes camera, video camera and microphone.

The large case was burned for 5 minutes; a violent combustion was not observed. The combustion was similar to the slow combustion of paper caps.

(b)Preparing test of a package of five large cases

The test conditions were similar to that used for the one large case.

When only light oil was used as heating fuel, there was noignition. Adding gasoline into the fuel was attempted but the package could not be well heated because of a strong wind. After burning oil, the package burned intermittently for 15 minutes. In this situation the paper caps did not burn violently.

(A)practical test of three packages of five large cases

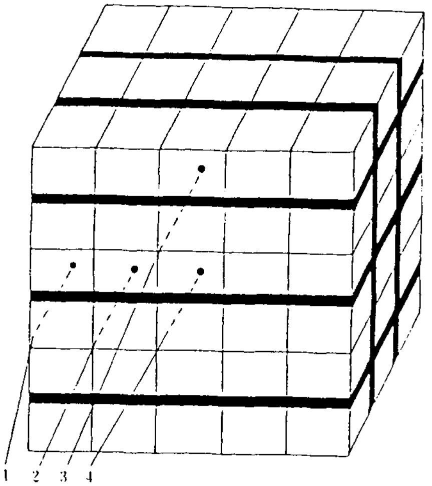


Fig. 5.14 Position of thermocouples for the external fire test

Except for using 20 liters of water, 20 liters of light oil and 2 liters of gasoline, all test conditions were similar to the previous test. The thermocouples were placed as shown in Fig.5.14 and the thermal history was recorded. The preparation and test sites are shown in Fig.5.15 and Fig.5.16. Because of wind the oil could not strengthen the combustion. The external fire test for 15 large stacked cases did not very markedly. After combustion flying fragments were not observed. Thermal histories are shown in Fig.5.17. Because the thermocouples were located between two large cases, the maximum temperature was about 800 ℃ ; this was not the temperature of flame. The primery burning substance could have been the corrugated boad, which could not achievea high temperature.

Fig. 5.15 Preparation for the external fire test

Fig. 5.16 The external fire test of 3 packages of large showing the of oil and the packages after 3 minutes of ignition

5.2.11 Summary

The package methods, in which a small case containing three sheets of corrugated boads used as shock-absorbing material was inserted between small cases of sporting signal paper caps, and the UN one package and stacked packages tests were carried out. In these tests No.0 detonators were used as ignition sources and only burning or explosions near the detorator occurred no propagation of explosion or more exfenine burning were observed.

In the UN external fire test, packages of paper caps burned slowly but not violently. Therefore, the modified package methods of sporting paper caps can be considered safe. From these test results the packages of paper caps do not belong to the highly dangerous classification and can be classfied in the dangerous region as 1.4s.

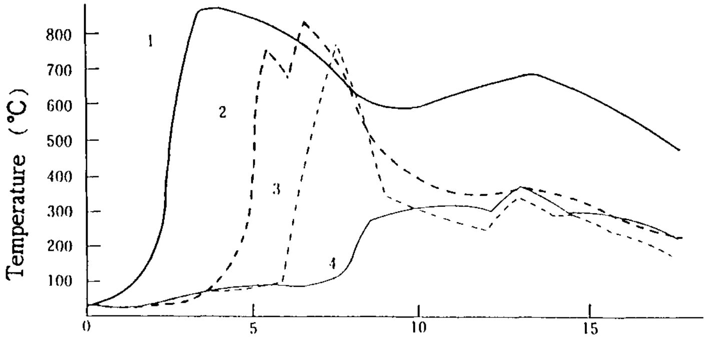


Fig. 5.17 The thermal histories from the external fire test for 3 packages of 5 large of sporting paper caps

5.3 How to build a safety storage shed for small amounts of explosives.

5.3.1 Introduction

At present the first precaution to take for storing explosives safely in an urban area is to secure the area from theft. The second consideration is to prevent damage to the surroundings, since accidents may happen unexpectedly. It is also most desirable that the sound of any explosion be small enough so that little or no anxiety will result on the part of neighbors from an explosion.

A temporary storage shed which meets the above requirements has the potential of being utilized widely as a storage facility for explosives and related articles at construction sites. At present,communication systems in big cities are already saturated and clogged, and the redevelopment of cities and exploitation of a deep underground subway system will be the reality of the near future. These changes will require explosives to be maintained at construction sites safely.

The following considerations were suggested when the development of a safe storage shed was discussed.

(1) The quantity of explosives to be stored should be kept to a minimum in each unit.

(2) If one unit explodes, the propagation of the explosion to other units should not be possible. This idea stems from experience. Safety wrapping was used in the casing

of paper percussion cups used at sporting events and described in Section 5.2 as a small scale approach to managing this same concern.

(3) Even if one unit explodes, there should not be substantial damage to the shed itself. Therefore no visible outside damage should result from any explosion within.

(4) Even if one unit explodes, the sound of the explosion should not be so loud as to cause anxiety for the people in the surrounding area.

(5) In case of fire, the storage shed should be tough enough to resist the heat of the fire so that the explosives inside will be protected from detonation.

To address these concerns, the following organizations experimented independently and also cooperatively: The National Association for Safety with Gun Powder, the Japanese Merchants' Association for Firearms and Gun Powder, the Yoshida Laboratory at the University of Tokyo, the Kobayashi Laboratory at Chuo University, and the Shirakawa Manufacturer at the Nippon Machinery Company.

5.3.2 Buffer materials to ease the effects of shock waves and the safest distance between units to prevent the propagation of explosion.

When a single piece of explosive detonates in a storage shed, two things need to be considered: the properties of the materials used to isolate the units where explosives are housed, and the distance needed between the units to prevent propagation of the explosion.

The effect of buffer materials is to soften shock waves. The safety wrapping technique for paper percussion cups which are commonly used to start sports events was tested by exposure to a weak shock wave. The small gap test (II) (Sec.5.2.3 in this book) was used. A propagated explosion test using a strong shock wave was also tried in sand (Sec.3.8.3). As a result of these tests, it was found that river sand was a practical material that could be used to soften shock waves.

Before the critical distances for the propagation of explosions in sand are measured, one must find one of the most sensitive explosives in use today. If one knows the distance needed between two samples of this most sensitive explosive to insure that no propagation takes place, other less sensitive explosives will not experience propagation of explosions if separated by this critical distance.

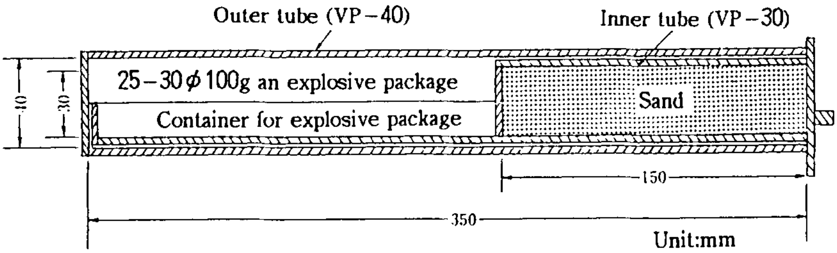

Outer tube (VP-40)
Inner tube (VP-30)
25-30φ100g an explosive package
Container for explosive package
Sand
40
30
150
350
Unit:mm

Fig. 5.18 General drawing of a single container

Identification	Size (mm)		
	Outer diameter	Inner diameter	Thickness
VP 30	38	31	3.1
VP 40	48	40	3.6

The shock sensitivity of industrial explosives which are in use today has been measured by a variable initiation test using a MKIII projectile mortar and a small gap test (Sec.3.7.4). No. 2 Enoki dynamite was found to be the most sensitive among the industrial explosives now in use.

Next, a propagating explosion test was carried out as a preliminary examination. Two packages of dynamite in vinyl tubes were laid separately in sand. One was a donor, the other the acceptor. It was found that if the donor dynamite was initiated, the acceptor did not explode when the distance between the two samples was approximately 10cm. After this test, a propagation test in sand was carried out (Figure 5.19) with one explosive in a vinyl tube 30mm in diameter and another as a single package of explosive (Figure 5.18). If the distance between them was 150mm, it was concluded that no propagation of explosion occurred after initiation by a donor industrial explosive.

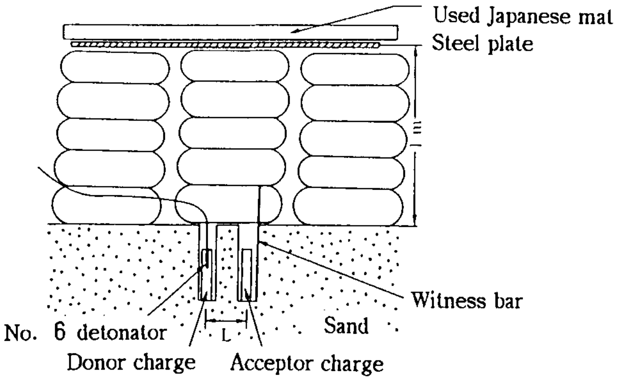


Fig. 5.19 Arrangement for test of sympathetic detonation for dynamite in vinyl chloride tube buried in the sand

Throughout these experiments there was complete agreement between the results obtained from the propagating explosion test and the sequence of sensitivity for industrial explosives determined using a MKIII projectile mortar: No. 2 Enoki Dynamite > No. 3 Kiri Dynamite > Energel MA−7 > Black Carlite > Iremite ≑ Ammon Explosive > Hamamite > Ammonium Nitrate Oil Explosive.

The explosives in the parenthesis were not examined by the propagating explosion test in sand. Table 5.6 shows the results of that test.

Because there are about 100 No. 6 detonators in the storage shed in question as well as other explosives, the propagation of explosions in sand was examined for detonators and dynamite. Fig. 5.20 shows that the samples were laid in the sand. In spite of the initiation of detonators, the dynamite did not propagate an explosion. The dynamite was in vinyl chloride tubes (VP−30), and these tubes were not damaged. This demonstrated that there were only small shock waves felt against the tubes.

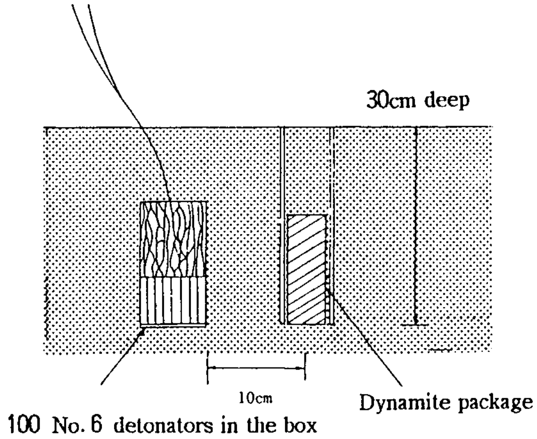


Fig. 5.20 Sympathetic detonation in the sand for dynamite initiated by 100 detonators

Table 5.6(a) Data for the propagating explosion test in sand using packages of explosives.

Explosive (30mm in diameter, 100g in weight)	Distance between packages in center (cm)	Testing results
Energel MA-7	10	× × ×
	8	× × ×
	7	× × ×
	6	○○○
No. 2 Enoki Dynamite	12	× × ×
	10	○○○

Table 5.6(b) Data from the propagating explosion test in sand using explosives in a VP30 vinyl chloride tube.

Explosive (30mm in diameter, 100g in weight)	Distance between packages in center (cm)	Testing results
Energel MA-7	10	× × ×
No. 2 Enoki Dynamite	12	× × ×
	10	○ × ×

Table 5.6(c) Data for the propagating explosion test in sand using explosives in a single package.

Explosive (30mm in diameter, 100g in weight)	Distance between packages in center (cm)	Testing results
Energel MA-7	10	× × ×
No. 2 Enoki Dynamite	12	× × ×
	10	○ × ×

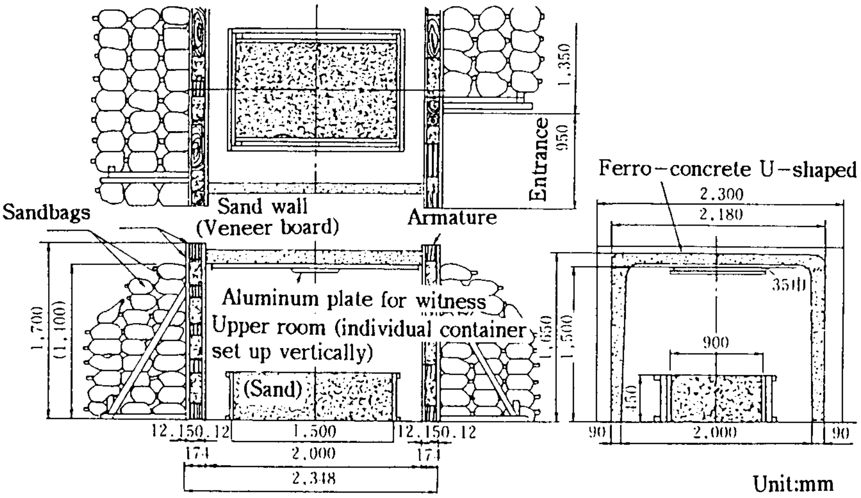


Fig. 5.21 General drawing of the mock storage house (I)

5.3.3 An explosion test inside a storage shed using a model shed (I) for small amounts of explosives.

We concluded from the experiment described above that if any one packaged explosive happened to explode, it did propagate the explosion toward other explosives if they were packaged individually with a 15cm distance between each other in the sand. A model of a storage shed was then constructed in the sand and exploded. The extent of damage to the model and the amount of noise produced by the explosion inside the model were measured. Fig. 5.21 shows a general view of the model storage shed. An L–shaped receiving room was prepared as one of the rooms in the sand (Fig 5.22 and 5.23).

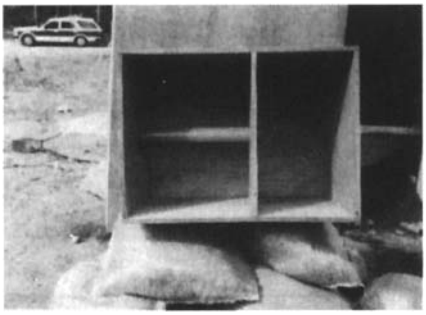


Fig. 5. 22 Photograph seen from top of L–shaped room without sand.

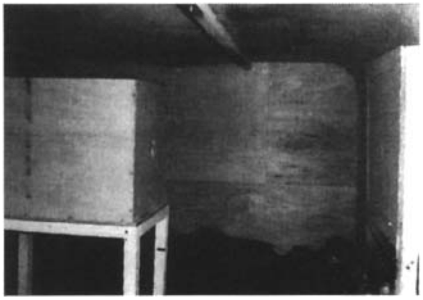


Fig. 5. 23 L–shaped room (left) and concrete witness board (right) set up with one single container.

The damage was examined by checking witness plates made of aluminum with a thickness of 1mm and 3mm and a ferro–concrete plate approximately 50cm × 50cm × 3.0cm. The speed of the projectile that exploded in the sand was not as fast as first expected. The explosion did not cause any serious damage to the surroundings. The storage building and others were seriously damaged by the shock wave from the explosion. The receiving room in the storage shed, however, was damaged by the explosion of one piece of packaged explosive. The effects of sound will be discussed later.

5.3.4 An explosion test inside a mock storage shed (II) with small amounts of explosives.

After a thorough examination of the mock storage shed (I), the role of the storage shed was clear. We then built a mock storage shed to scale and tested it by initiating an explosion inside the structure. It was confirmed by the measurement of ground vibration and the sound of the explosion that the storage shed met our specifications.

The dimensions of the mock storage shed (II) are: 2.2m wide, 2.2m deep, 2.3m high, with an outside wall 10cm thick. This structure is shown in Figures 5.24 and 5.25. It has a steel door (0.81m × 1.8m, 4.5mm in thickness) and a ventilator (200mm × 250mm, with a steel fire door). The fire door is insulated with sand 15cm thick to prevent noise from escaping.

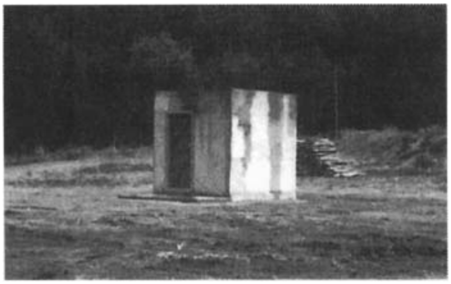
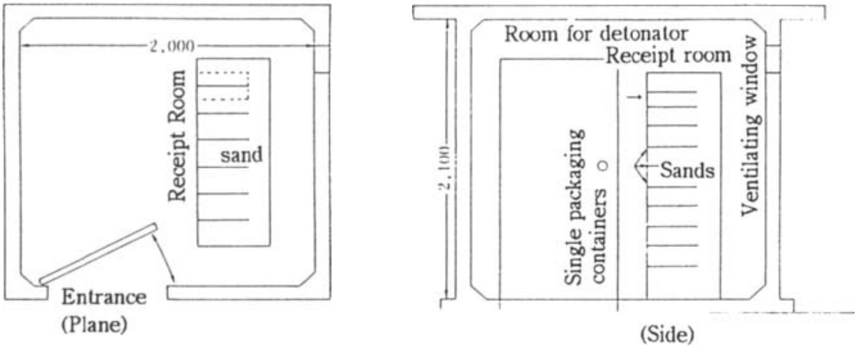


Fig. 5.24 View outside of storage house(II) with small amounts of explosives



Unit: mm

Fig. 5.25 General drawing of the storage house

An open receiving room (1m × 1m, 50cm in depth) filled with sand was included as a mock receiving room. For measuring acceleration,ground vibration and the sound produced by the explosion, sensors were placed at various points as shown in Figure 5.26. No damage was noticed inside the mock shed.

5.3.5 The sound of the explosion*.
(*: sound analyzed by Mr. Eishi Kuroda and Prof. Naota Kobayashi)

(1) The sound produced by an explosion in and on sand.

For each package of Energel MA−7 30mmS(100g in weight), the sound produced by its explosion was measured under six different sets of conditions. Table 5.7 shows the results of the tests. The values were calculated by taking the average of three measurements.

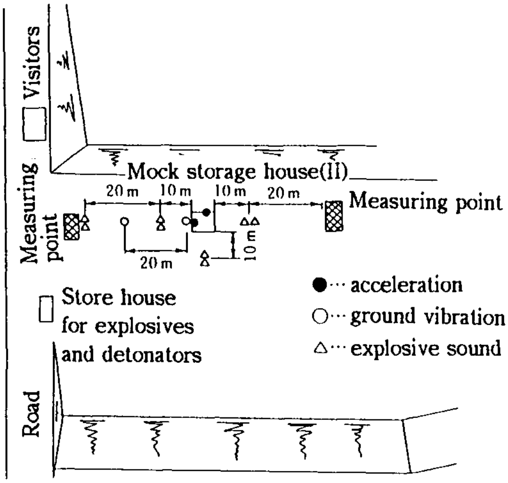


Fig. 5.26 Measuring position for each data point

(a) The explosion on sand.

(b) VP−30: A VP−30 vinyl chloride tube 30cm in length with the bottom of the package of explosive filled with sand was buried in the sand such that the top of the tube was at the surface.

(c) The explosion in the sand: The package of explosive was laid in the sand horizontally 30cm deep and was exploded.

(d) A single container 30cm in length without a sand filling was exploded as follows: the container was buried in the sand vertically with the upper end of the tube at the surface.

(e) A single container 30cm in length with a sand filling was exploded as follows: a single container similar to (d) filled with sand (10cm) was buried in the sand vertically with the upper end of the tube at the surface.

(f) A single container 35cm in length filled with sand was exploded as follows: the single container filled with sand (15cm) was buried in the sand vertically with the upper end of the tube at the surface.

The sound produced by the explosion was less in the single container with a 15cm filling of sand than in the one with a 10cm filling of sand. The sound was almost the same for one with a 10cm sand filling as for one without any filling. The facts are as follows: the filled sand 10cm in length was ejected like a shell shot from a gun, but the sand filled to a level of 15cm was not ejected. The energy of the gas produced by the explosion was transferred into the sand.

Table 5.7 The sound produced by explosions under various conditions (dB).

Measuring points	100m			350m	
Condition of explosive / Special character.	Flat imp	Linear imp	A imp	Flat imp	Linear slow
On the sand	119.5	118.0	01.5	99.5	75.0
VP-30	110.0	111.0	84.5	89.0	59.5
In the sand	97.0	104.5	70.0	79.0	68.0
30cm single container without filling	109.5	105.5	93.5	89.5	72.5
30cm single container filled with sand	109.0	105.5	93.0	93.5	73.5
35cm single container filled with sand	102.5	101.5	85.0	84.0	68.0

Notes: The impulse level values are read by a High Speed Graphic Recorder LP−50. Linear slow values are read by VM−14B. Differences commonly used between impulse level and first level are 3.5−4.5dB.

In the case of exploding a 15cm single container filled with sand,the sonic pressure and noise were less than 15dB. Comparing this single container's explosion with the detonation of an explosive buried in the sand at a depth of 30cm, the sonic pressure was higher because it was not buried. Its noise level was also much higher because of the effect of the open space surrounding the package.

Table 5.8 Results of the explosive sound for No. 2 Enoki Dynamite (dB).

Run	10m from sand wall		10 m from concrete wall		50 m from concrete wall	
No.	A	L	A	F	A	F
4-7	100-101	96-97	106-113	102-108	76-89	86-91
8	106	101	117	113	92	98
14*	107	102	110	113	90	97
9,10,15	100	96-102	109-114	107-109	85-87	87-97
12	110	109	117	114	91	96
13,16-18	121-127	117-118	122-125	124-130	104-110	109-120
19	125	118	125	-	110	118

*: There was a space between the sand wall and the concrete construction.

A: a special characteristic, L: a linear special characteristic, F: a flat special characteristic.

(2) The sound of an explosion in a mock storage shed (I).

Table 5.8 shows a summary of the results of the sound of explosions measured at the mock storage shed. Data is shown at the impulse level, and data from the fast level is usually 3.5−5.5dB lower than the impulse level data. Impulse levels were used for the dB values. The frequencies used for a linear response were 1−90Hz for the special linear characteristic and 10−20Hz for the special flat characteristic. In many cases the explosive sound was measured over 100Hz to include the main components. One must pay close attention to methodology when comparing and analyzing measured values of sounds.

A single container of explosive was buried in the sand right side up in the center of the open receiving room. It was filled with about 175g of explosive, topped with a 15cm length of sand, and was then exploded. The differences between the sound produced by this explosion and the other explosions under different conditions are shown in Table 5.9.

Table 5.9 Difference of the explosive sound (dB) in a mock storage shed (I).

Run	10m from sand wall		10 m from concrete wall		50 m from concrete wall		Test conditions
No.	A	L	A	F	A	F	
4-7	0	0	0	0	0	0	100g, V.S.
8	5.5	4.5	8.0	7.0	10.7	10.2	100g, V.NS.
14	6.5	5.5	1.5	7.0	8.2	9.2	100g, V.S.G.
9,10,15	-0.5	2.2	3.2	2.5	4.5	3.9	100g, H.S.
12	9.5	12.5	8.5	8.5	9.7	8.2	300g, V.S.
13,16-19	24.5	21.0	15.4	11.6	25.7	25.6	100g, SS.

Note: V.:Vertically; S.:Sand filling; NS.:No Sand filling
H.:Horizontally G.:Gap; SS.:Surface of Sand

When no sand was filled in and the explosion was measured at a 10 m distance, the noise was 5.5−8dB higher than when the container was filled with sand. The sonic pressure (flat or linear special characteristic) was 4.5−7dB higher than when the container was filled with sand. At the 50m point, both the noise and the sonic pressure were about 10dB higher than when the container was filled with sand. The sound in the receiving room was 0−4.5dB higher when the explosive was horizontal than when it was vertical. While the energy generated by the explosion was released in six directions for the horizontal explosive, the explosive energy in the case of the vertical explosive was released only in a vertical direction. The energy of the sound source decreased and the intensity of the sound was weak. When three pieces of dynamite were exploded simultaneously in a single container with a filler, the results of measurements of sonic pressure and noise were considerably higher at 8.2−12.5dB, three times the sound intensity of an explosion with one piece of dynamite. In the case of the simultaneous explosion, the sand was easily blown away because the energy that is the source of the sound increased.

Table 5.10 shows the conditions of the experiment using a mock storage shed (I).

Table 5.10 Experiments in a mock storage shed (I). Using No.2 Enoki, 30 ϕ

Ser. No.	Run No.	Date & time	Conditions of explosion source		
			Vessel	Sand Filler	Weight(g)
01	Reserve1	10/30 14:40	vertically in a single container	w/	(detonat)
02	Reserve2	10/30 15:00	vertically in a single container	w/	30
03	Reserve3	10/30 15:30	vertically in a single container	w/	60
04	Reserve4	10/30 16:00	vertically in a single container	w/	100
05	1-1	10/31 09:55	vertically in a single container	w/	100
06	1-2	10/31 10:20	vertically in a single container	w/	100
07	1-3	10/31 10:55	vertically in a single container	w/	100
08	1-4	10/31 11:25	vertically in a single container	w/o	10
09	2-1	10/31 13:20	horizontal in a single container	w/	100
10	2-2	10/31 13:40	horizontal in a single container	w/	100
11	1-5	10/31 14:20	vertically in a single container	w/	100
12	3-1	10/31 14:50	vertically in a single container with 3 sticks of dynamite	w/	100
13	4-1	10/31 15:25	On sand	-	100
14	1-6	11/01 09:10	vertically in a single container	w/	100
15	2-3	11/01 09:40	horizontal in a single container	w/	100
16	4-2	11/01 10:05	On sand, 92cm from wall	-	100
17	4-3	11/01 10:15	On sand	-	100
18	4-4	11/01 10:35	On sand	-	100
19	4-5	11/01 10:50	On sand, 15cm from wall	-	100
20	4-6	11/01 11:05	On sand, stuck closely to wall	-	100
21	4-7	11/01 11:20	About 30cm deep in sand, stuck close to wall	in sand	100

(3) The explosive sound in a mock storage shed (II)

The immediate interest for testing a storage shed with small amounts of explosives was to determine if noise and sonic pressure decreased outside the storage shed when a single container filled with sand was exploded in the sand in a receiving room in the storage shed. Table 5.11 shows the results of measuring this relationship.

Under the conditions indicated in the table, 1B−100 and 1C−100 show the results of the explosion of a 100g explosive package in a single container filled with sand as measured at the receiving room above and to the side of the container in the absence of a sand wall. Condition 2B−100 has no a sand wall. Conditions 1B Dry−100 and 1B Wet−100 are filled with dried sand and sand saturated with water respectively.

Table 5.11 Sound from the explosion of a single container.

Characteristic		A	Flat			Linear		
direction	Ventilat. dir.	Door dir.	Double steel wall dir.	Ventilat. dir.		Door dir.	Double steel wall dir.	
Distance(m)	30	10	30	10	30	10	10	30
Sound source condition								
1 B-100	96.3	105.3	86.0	113.8	107.0	109.5	--	93.8
1 C-100	97.5	106.3	85.3	114.3	107.0	114.8	--	97.5
2 B-100	97.5	106.8	82.2	113.2	106.2	110.2	102.5	97.5
2 C-100	96.2	101.5	85.7	116.3	109.5	108.8	102.5	102.5
1B Dry-100	96.8	--	85.5	--	107.3	105.5	100.8	94.0
1B Wet-100	91.0	--	81.8	--	105.3	103.8	99.5	91.5

The units for the values in Table 5.11 are shown as dB A impulse for A, dB F impulse for flat, and dB L impulse for linear. One must pay attention when using a super low frequency sound meter to the linear reading. The linear range of its dynamic response is 1−90Hz; when the frequency component is over 90Hz, it becomes a low level frequency.

The sound meter was not able to measure completely the sound going in three directions; hence, the sound intensities in each direction could not be directly compared. However, regarding an analysis based on a reduced distance (the difference in a frequency component caused by distance and direction), it may be understood in the following manner:

The ventilation direction is highest at 10 m according to the noise and sonic pressure level, and lowest in the direction of the door where there is a the double wall. At 10m from the storage shed, the A characteristic impulse level is 110dB, and the Flat impulse level is not over 120dB. At 30m, the A characteristic impulse level is 100dB, and the Flat impulse level is not over 110dB.

Environmental influences were discussed from the data based on the results. The relationship between noise level and human reaction based on a formal questionnaire is as follows:

Over 115dB A fast....cannot stand it without covering ears.

90dB A fast..........complaints were frequent.

70dB A fast..........complaints were rare.

According to the measurements, at a distance of 10 m the noise level was not over 110dB A imp (about 106dB A fast), which is sufficiently less than 115dB A fast.

Therefore sound at this level can be tolerated by a person without covering the ears. At 30m it is less than 100dB A imp (about 96dB A fast), which is over 90dB A fast, which may result in complaints. However, the questionnaire asked about sounds rated at 90dB A fast and repeatedly heard many times a day. In the case of this storage shed, it only exploded accidentally once. Therefore, a person may only be surprised by the sound of the accidental explosion. This single sound should not cause any problems.

At a distance of 10m from the highest positioned ventilator, the sonic pressure level is under 120dB. Although the safety limit for the impulse noise is 140dB L fast according to OSHA and 141dB L peak according to CHABA, the sonic pressure level measured under these conditions is low enough. There should definitely be no effect on the ears.

The sound outside the storage shed was made by the vibration of a wall and the steel door, and by a gas emission from a gap between the ventilator and the door. In trying to reduce the sound from the storage shed, the source of the explosion had to be considered; using a filler of sand is the first method to reduce the sound, and for better results, sand saturated with water should be used.

There are all kinds of soundproofing countermeasures −using buffering materials to prevent shocks to the door, preventing gas emissions,affixing buffering materials to the inside walls, mounting a reflection plate for the ventilator, and hanging a metal screen were all recognized to be effective. However, the effectiveness of each of these devices was very complicated to assess and varied with respect to the source of the explosion and its direction.

The effectiveness of a sand wall was not unique; it varied with the source of the explosion and its direction, but it was generally a good buffer except in the direction of the door. Of the horizontal and vertically receiving room, the former was higher in noise and sonic pressure and was the highest by about 5dB in the direction of the door.

5.3.6 An outside experiment with a fire for a mock storage shed (III) containing a small amount of explosives.

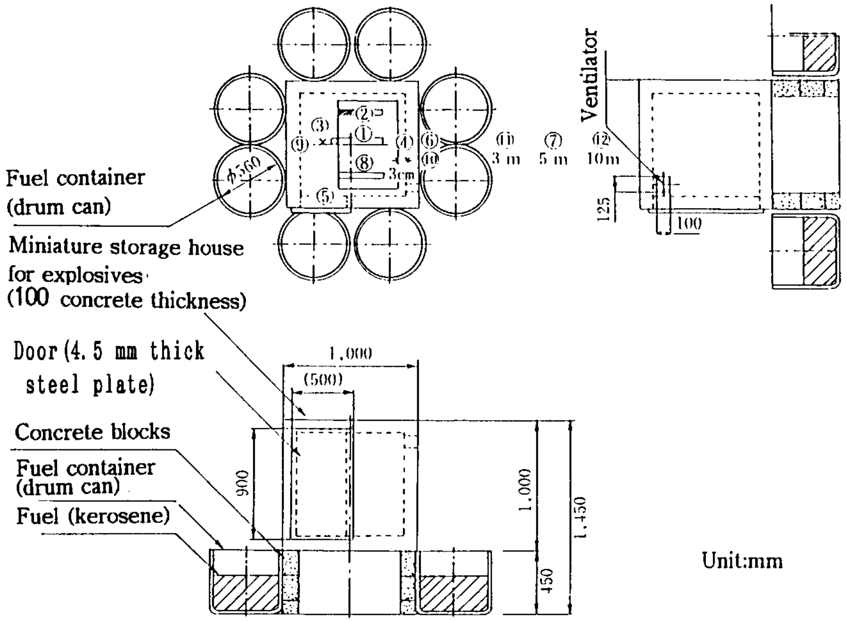
In this section we assumed there was a fire near the storage shed. We measured the temperature in the storage shed when a fire occurred outside.

(1) Mock storage shed (III)

Figure 5.27 shows a drawing of a mock storage shed and a drawing of the location of an outside fire. The purpose of the experiment is to determine an interior temperature within the mock storage shed during a fire outside the shed. However, an actual sized mock storage shed was difficult to experiment with, so a half−scale one was used. We used a similar sized wall in the mock storage shed −−a reinforced concrete wall

10cm thick -- and a 4.5mm thick steel plate door.

The experiment was done three times. In the first and third experiments, fireproof materials were attached to a steel plate which was used as a door, and the opening was filled with asbestos cloth. The ventilator was covered with an insulating plate.The specifications of the mock storage shed (III) are as follows:



①②⑧ are in the single packaged container.
③ is the central point of the area.
④⑨ are touching the wall.
⑤ is touching the door.
⑥⑩ are 3 meters from the surface of the central wall.
⑪⑦⑫ are 1 meter high.

Fig. 5.27 Drawing of the mock store house (III) and general view of the outside fire experiment

(a) Dimensions

1m wide × 1m deep × 1m high. Size of(II) is 2.2m × 2.2m × 2.3m; this is almost half-scale.

(b) Thickness of the concrete wall:

10cm

(c) Door:

Thickness was 4.5mm; covered with a steel plate.

(d)

Opening 100 × 125mm. 1/2 scale of (II), and the space behind the screw was

25mm for each nut used to secure the steel plate.

(Note) The process of opening and closing the door and the ventilator were not supposed to influence the temperature measured in the experiment; therefore, the steel plate used as a door was bolted into place.

(e) Fireproof insulation materials:

Siborex 50 (the most popular and high quality) was used.

The Siborex was attached by bolts on all steel surfaces of the outer side of the door and ventilator. The Siborex used was 50mm thick.

(f) Receiving room:

600mm wide × 500mm deep × 500mm high; it was made of veneer board 12mm thick.

The actual length of the single container was 350mm, 150mm of which was filled sand. The receiving room was located in its proper position in the storage shed and had inside dimensions of 800mm × 800mm × 800mm.

Three single containers were fixed in position with reference to the exterior of the tubes as shown in Figure 5.26. Since the receiving room could not fit through the entrance of the storage shed, the back half and front half of the room were built and then reassembled in the shed and filled with sand after the shed was built.

(2) Sham fire

A torch was used to cut a 200 litre steel drum can in half. Eight pieces were used in all. Their depth was 450mm.

Eighty liters of Kerosene filled each container to a depth of about 325mm. The total amount of oil used was 640 liters. Cloths were dipped partially into the oil so that they could be easily ignited. Five minutes before ignition, gasoline was also spread on the cloths.

A 100 volt nichrome resistance wire was used to ignite the soaked cloths at four ignition points. Eight cut drum–can halves were connected by the gasoline soaked cloths. (Refer to Figure 5.29)

(3) Measurement of temperature

The temperature was measured by twelve thermoelectric couples and was recorded by two multilogers. The places where the temperature was measured are shown in Figure 5.28. The recording devices and the positions of the thermocouples for each recorder were connected as follows:

A Multiloger

7ch	Center of the single container
8ch	Other side in the single container
9ch	Center of the storage shed
10ch	Touching the wall at the bottom of the receiving room
11ch	This side in the single container

12ch Face of the wall in the center of the storage shed

B Multiloger

7ch Touching the steel plate door

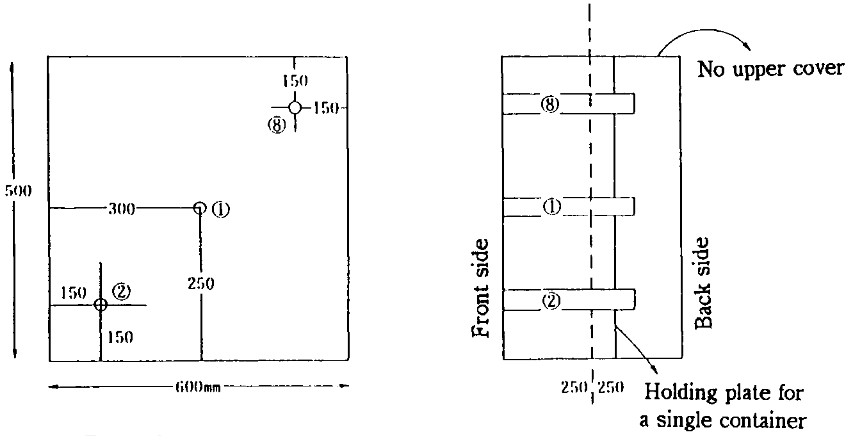
8ch 3m from the center of the wall outside the storage shed

9ch 5m from the outside wall of the storage shed

10ch 3m from the center of the wall outside the storage shed

11ch 5m from the outside wall of the storage shed

12ch 10m from the outside wall of the storage shed



Front view of front side

Unit:mm

(It was cut at the dotted line, put together with adhesive and metal cord, then the single container set up and sand put into the room. The numbers in circles show the positions of thermocouples.)

Fig. 5.28 General drawing of the room

(4) First experiment with a fire outside the storage shed

The lead wires of the thermocouples overheated during the first experiment.

(5) Second experiment with a fire outside the storage shed

The temperature inside the steel plate door reached 660, and it was realized that an insulator was needed on the door.

(6) Third experiment with a fire outside the storage shed

Figures 5.30–5.33 show the temperatures measured.

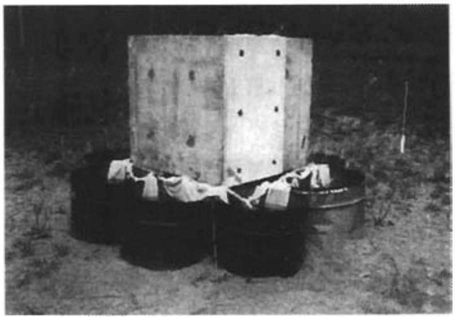


Fig. 5.29 The mock storage house (III) coated with fire–proof board on the surface of steel board.

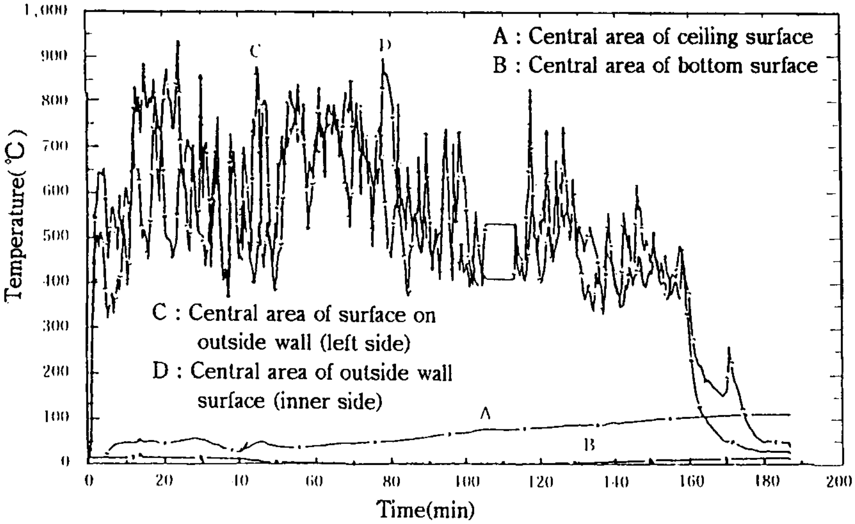


Fig. 5.30(a) Temperatures from the outside fire experiment No. 3 − 1.a.

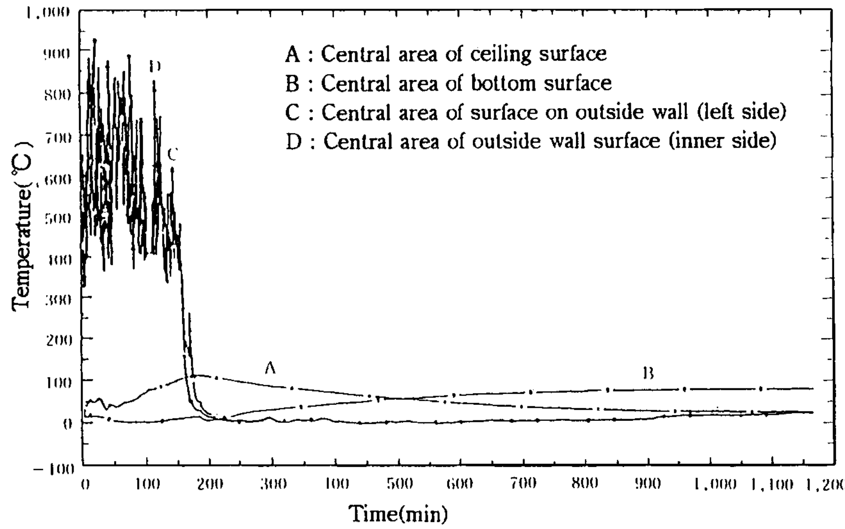


Fig. 5.30(b) Temperatures from the outside fire experiment No. 3 − 1. b.

Because we were unsuccessful in performing the first experiment, the third experiment was necessary. After the second experiment, the insulation on the door was attached inside the door instead of outside.

The only other difference in the way the third experiment was carried out compared to the first was that a hole was drilled in the center of the wall of the storage shed. A thermocouple was set up 5cm inside the concrete wall for measuring the temperature.

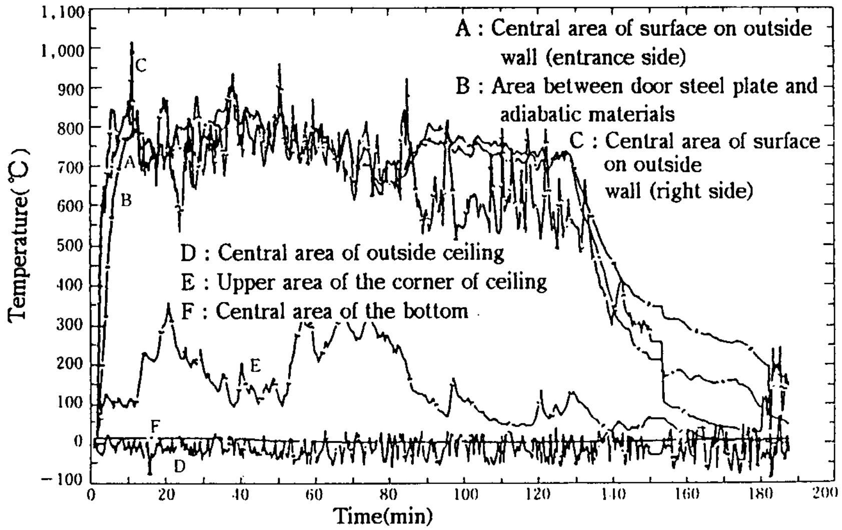


Fig. 5.31(a) Temperatures from the outside fire experiment No. 3 − 2.a.

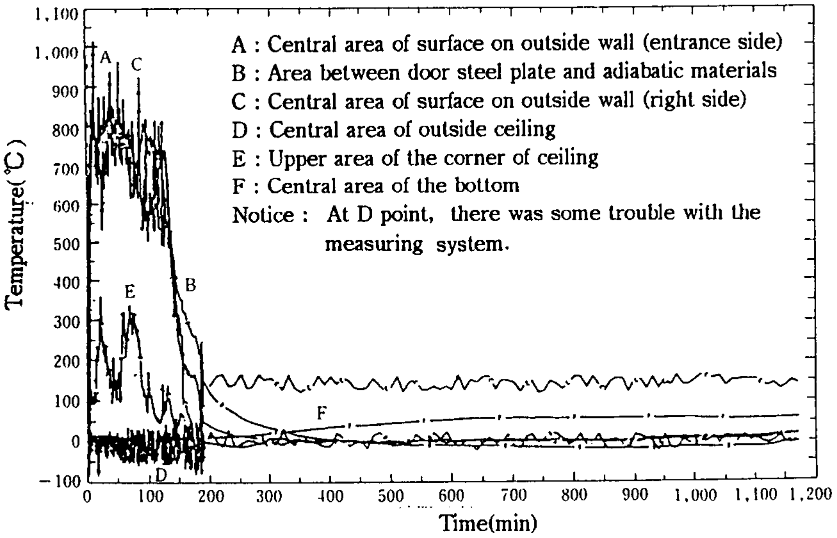


Fig. 5.31(b) Temperatures from the outside fire experiment No. 3 − 2.b.

(a) The face of the outside wall of the storage shed

In the first and second tests the positions where the temperature was measured were 3cm from the outside wall; in the third one it was measured adjacent to the wall. The four faces of the walls, including the wall with the door, registered temperatures at wide ranges as shown in Figures 5.30 and 5.31. Recorded values were 800−900 at maximum and 600−750 at median values. Between 130 to 150 minutes after ignition,

the temperatures rapidly decreased. The total burning time was 120 minutes.
While the temperature continued to rise slowly to 110 at the ceiling face, the temperature of the steel plate door rose to the same temperature as the outside wall.
The wide range of temperatures measured by thermocouples attached to the wall was caused by the difference between the temperature of the concrete wall itself ——that was considered to be a comparatively low temperature—— and the temperature of a wall that was heated directly.

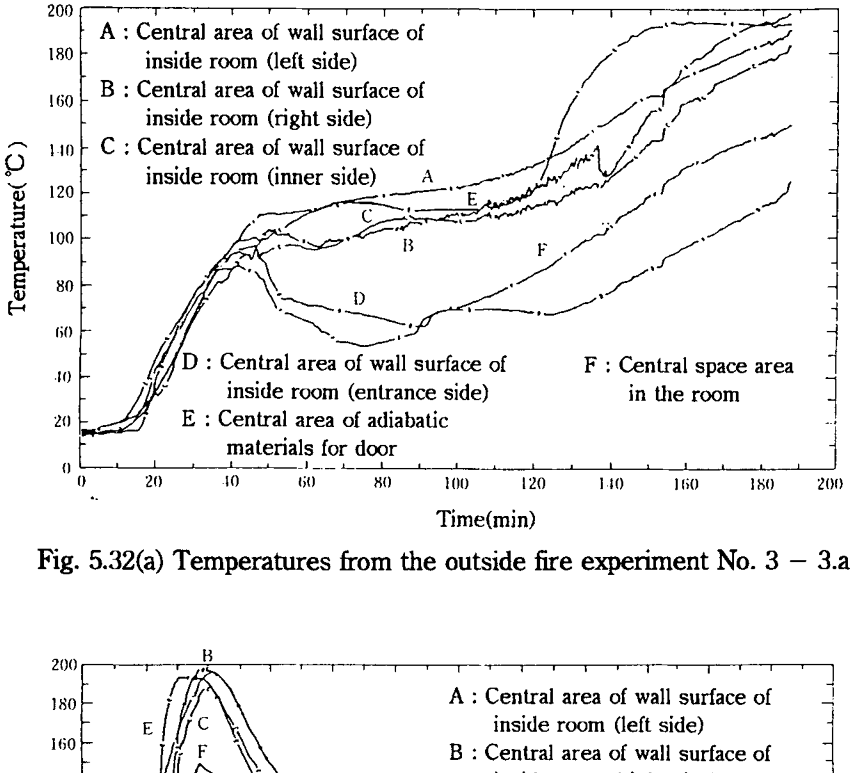


Fig. 5.32(a) Temperatures from the outside fire experiment No. 3 – 3.a.

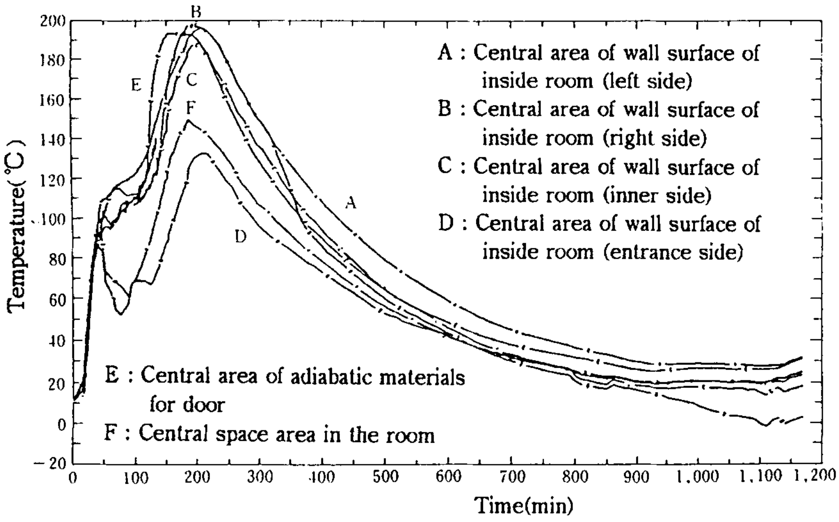


Fig. 5.32(b) Temperatures from the outside fire experiment No. 3 – 3.b.

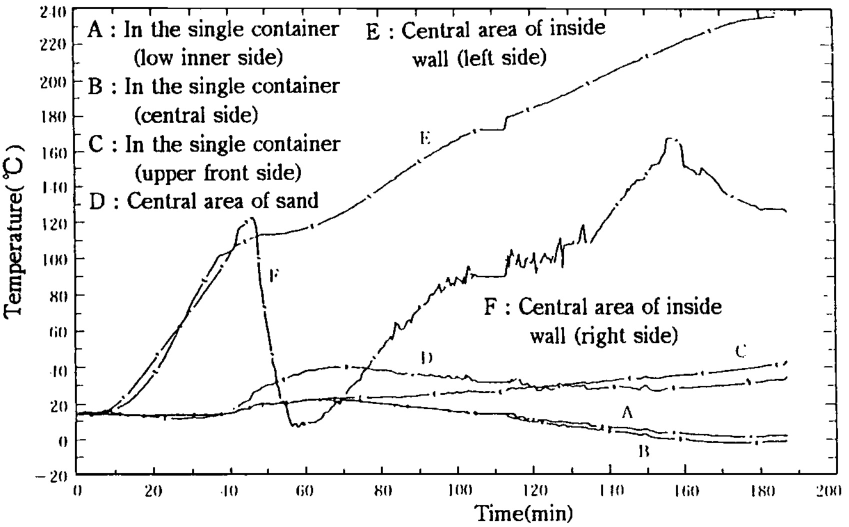


Fig. 5.33(a) Temperatures from the outside fire experiment No. 3 – 4.a.

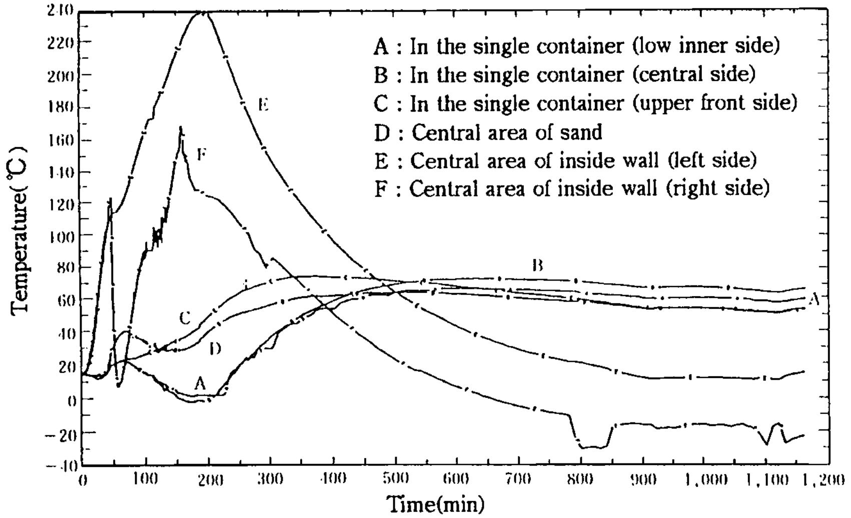


Fig. 5.33(b) Temperatures from the outside fire experiment No. 3 – 4.b.

(b) Face of a wall inside the storage shed

The temperature rose so quickly in the second experiment that 15 minutes after ignition it reached about 200 ℃ and held at 260–280 ℃ for 20–60 minutes. The temperature in the third experiment rose slowly (as shown in Figure 5.31), only reaching and then holding at about 40o for 40 minutes. It then continued to rise after the combustion ceased, attaining a high of 190–200 ℃ for 180–220 minutes.

Discrepancies exist between the second and third tests. The peak temperatures differed between 70–90 ℃ . The differences between the rates of temperature increase and between the maximum temperatures achieved were rationalized as follows: the insulator attached to the steel door, a good heat–conductor, was very effective, and the outside temperature when the experiment was run made a difference in the initial temperature of the mock storage shed itself.

(c) Inside of the body of a wall (5cm point)

The temperature was about 100 ℃ for 40 minutes after ignition as shown in Figure 5.32, and about 240 ℃ 190 minutes after ignition, which was a little bit higher than the inside wall temperature. The trend in temperatures inside the body of the wall was quite similar to that at the face of the inside wall. The temperature increase inside the body of the wall was thought to show the effects of heating by the outside face of the wall, which was 10cm thick. At measuring point F, its temperature decreased rapidly. But after the decrease, further temperature changes showed a trend similar to those measured at point E. There may have been some initial trouble with the measuring system, but it seemed to return to normal operation.

(d) Space in the storage shed

In the second test the temperature in the storage shed rose rapidly to about 110 ℃ five minutes after ignition; however, in the third test the temperature in the storage shed as well as the temperature at the wall rose more slowly. As shown in Figure 5.30,there was no change in temperature in the storage shed within 5 minutes after ignition; it rose to about 40 ℃ 20 minutes after ignition, and finally attained a high temperature range of 80–90 ℃ for about 34–45 minutes. Then it decreased continuously until reaching 55 ℃ about 75 minutes after ignition. Finally the temperature rose to its maximum value of about 150 ℃ approximately 150 minutes after ignition.

Once the elevated temperature inside the storage shed started to decline, it again rose back up to the highest temperature. This phenomena happened twice. In spite of reaching the high temperature of the outside wall of the storage shed, there may be a tendency to decrease in temperature temporarily after 30–40 minutes of combustion, followed by a trend in slowly rising temperatures at the inside wall of the storage shed.

(e) A single container in the room

A single container in the room, filled with sand and set away from each wall in the open space within the storage shed, was assumed to be fairly isolated from the influence of the fire outside.

Although the second and third experiments showed a similar trend, the third test showed that the rate of temperature increase was quite slow. The peak temperature at around the entrance occurred after 6 hours and at the center of the shed 6 hours later. Also the temperatures were as low as 60–80 ℃ as compared to 80–90 ℃ in the second test. At the center and in the interior of the room, the temperature first rose, then decreased, and then rose again. The cause of this behavior was understood to be due to heat conductivity and the presence of contained water.

Furthermore, once heated the temperature in the inner storage shed was maintained at 50−70 ℃ for up to 15−20 hours, as the inner storage shed was almost sealed and hence was capable of retaining heat.

(f) Storage shed after the fire outside

The storage shed was still standing after the outside fire ceased. There were no alterations; only part of the outer wall buckled. The inside of the storage shed did not appear to have changed.

5.4 Safety Evaluation of Gas Generators for Seatbelt Tensioners

5.4.1 Preface

Several explosive devices have recently been developed to enhance general safety. Some examples are air bags which protect the driver from injury in car collisions, and seatbelt tensioners which, when tied up with the action of an air bag, hold the driver to the seat. Explosives are also used as a source of shock waves in medical equipment for breaking up gall stones in a patient's body. In yet another application, explosives are used to generate shock waves in a patient's body water which are then focused on a kidney stone to break it.

Historically, explosives were invented in ancient China for use as a kind of "medicine with ignition quality", called 'fire medicine' in Chinese. But these devices are dangerous and can cause accidents. Therefore, safety evaluation should be carried out in parallel with their development.

The authors have participated in safety evaluations of imported air bags and seat belt tensioners and have acquired some experience in evaluating these devices. The authors conducted a safety evaluation of the gas generator used for seat belt tensioners developed by Pyro Safety Device Corp., cooperating with engineers from this corporation. The results of this evaluation are presented here, with the kind permission of the corporation.

5.4.2 Construction and composition of gas generator

The body of the gas generator is made of 22mm−diameter aluminum bar with a length of 45.5mm and a total weight of 32g, which is ignited by a special plug. Its construction is shown in Fig.5.34. It is charged with 0.9g of a gas−generating compound and 0.2g of an ignitor.

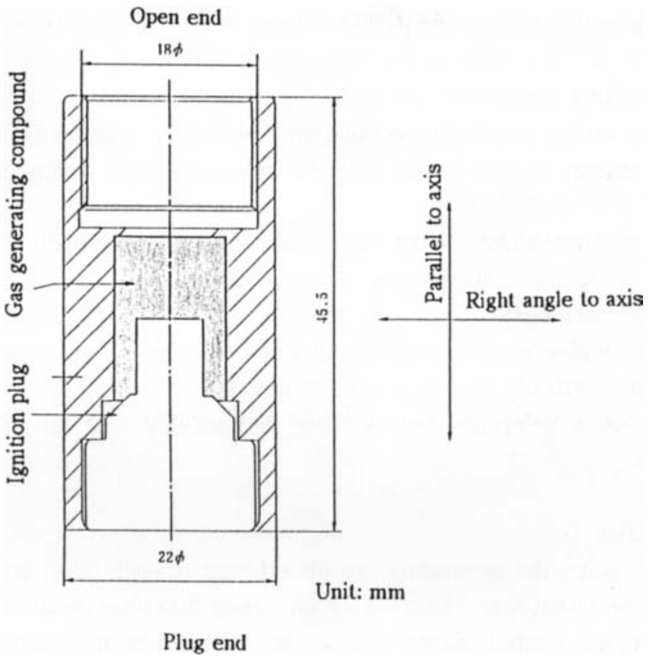


Fig. 5.34 Gas generator cross section

5.4.3 Name of tests and characteristics investigated

(1) Outer Shell Construction Test

To test the shell for strength to prevent its contents from spilling out.

(2) Normal Ignition Test

To investigate if the gas generator shell will break when ignited normally, and to measure the noise level range which is closely related to the sound pressure of explosions.

(3) Ball Drop Sensitivity Test

To investigate if a certain degree of impact will cause the gas generator to ignite and suffer serious damage and if the shell will maintains its original properties.

(4) Heat Test

To investigate if the gas generator will ignite when heated to a given temperature for a specific length of time.

(5) Vibration Test

To investigate if the original propertie of the gas generator will change after vibration at a given frequency for a specific period of time.

(6) Lateral Contact Test
To investigate, under more severe conditions, whether another generator will ignite when many generators are placed side by side (laterally) and one of them ignites accidentally.
This test is a reference test for the flammability test of individually packed generators.

(7) Vertical Contact Test
To investigate, under more severe conditions, whether other generators will ignite when one of the vertically placed generators ignites.
This test is also a reference test for the flammability test for individually packed generators.

(8) External Fire Test
To investigate, when the generators are placed next to each other and are accidentally surrounded by external fire, whether or not more than one generator will explode at the same time, or blasted pieces will scatter more than a certain distance, or the generators will intensify the surrounding fire.

5.4.4 Results of tests

(1) Outer Shell Construction Test
The shell proved to be very strong and could not be broken during normal usage. The generator was found not liable to misuse or abuse.

(2) Normal Ignition Test
(a) No damage was detected on the outer shell of the generator. It is highly unlikely that broken pieces would cause injury to people.
(b) Three noise levels at a distance of 50cm measured 129, 130, and 129 dB (A First), respectively.

(3) Ball Drop Sensitivity Test
(a) A 535g ball was dropped three times from a height of 20cm but no ignition occurred in the gas generators.
(b) No damage was observed to the generators.
(c) A normal ignition test was carried out on the drop−tested generators and, in all three tests, the noise levels were 129 dB.
The ball drop tester used is described in 4.3.1 of this paper, and the layout of the test is shown in Fig.5.35.

(4) Heat Test

None of the three gas generators ignited when heated at 80 °C for 8 hours. The test was carried out with an air-heated constant temperature chamber with air circulation.

(5) Vibration Test

(a) No ignition occurred during the test.

(b) No structural damage occurred.

(c) After the test, the gas generators underwent a normal ignition test. The noise levels were measured between 129 and 130 dB. Fig5.36 shows the layout of the vibration test.

(6) Lateral Contact Test

No other generator ignited.

(7) Vertical Contact Test

No other generator ignited.

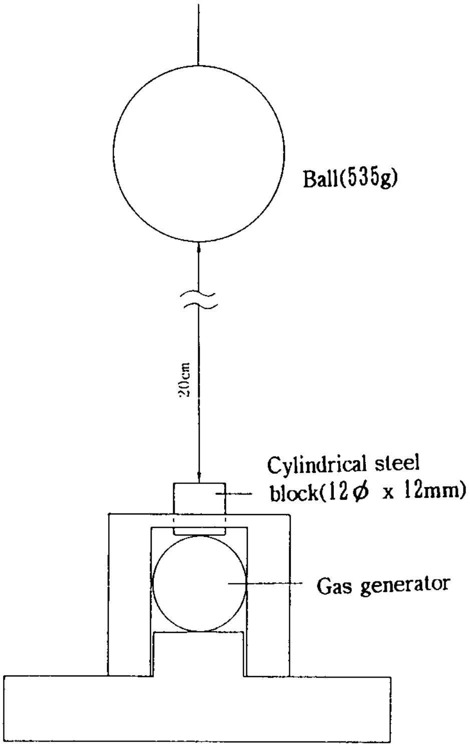


Fig. 5. 35 Layout of ball drop sensitivity test

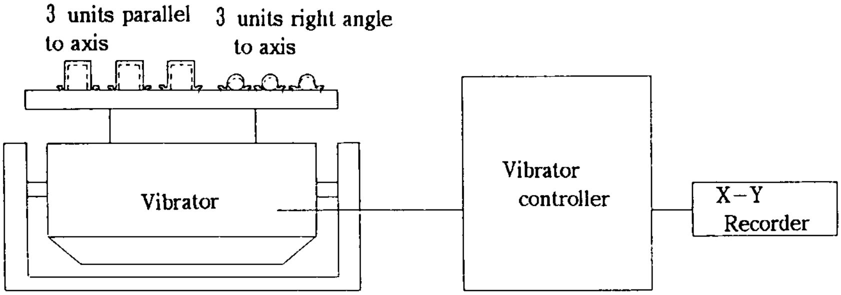


Fig. 5. 36 Layout of vibration test

The above lateral and vertical contact tests were conducted under more severer conditions than those in the individually packaged test. The layouts of these tests are shown in Figs 5.37 and 5.38. It is assumed that fire will not spread to other units when one of these types of gas generators ignites in a lot.

(8) External Fire Test

(a) The gas generators did not explode simultaneously.

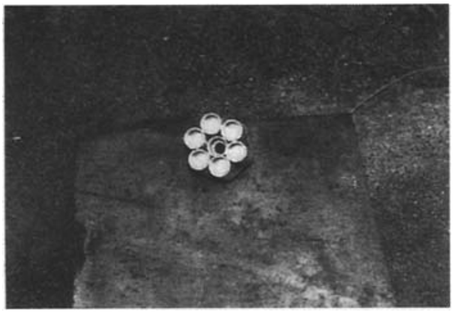
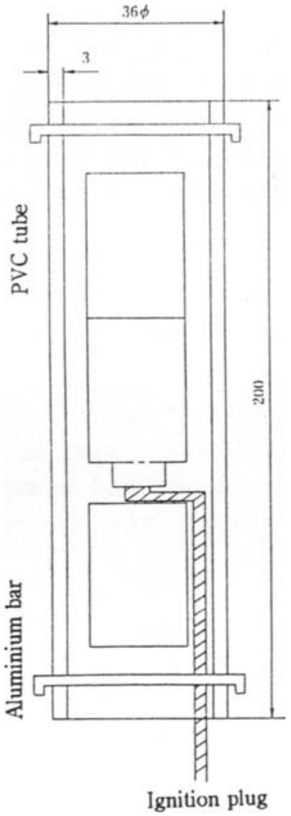


Fig. 5.37 Photo taken after gas generator lateral contact test (Only the ihnited generator shows results of reaction)



Unit: mm

Fig. 5.38 Layout vertical contact tester of gas generator

(b) Blasted particles fell within a 16m distance.
(c) The burning of gas generators did not intensify the burning of the railroad ties.

Photographs illustrating the External Fire Test are shown in Fig. 5.39 to Fig.5.42. Fig.5.39 is a photo which shows the inside of the test package. Three styrofoam plates, each containing 7 generators, were piled up with dummy plates on the top and bottom.

The generators were placed at the outer side in the package to ensure effective observation of the blast and the location where pieces would easily be dispersed by explosion.

Fig. 5.40 shows the arrangement of the test package and the fuel to make an external fire. From previous experience, we found that a combination of railroad ties, small pieces of wood, and a mixture of kerosene and gasoline is suitable for external fire tests. The sample was placed on top of the fuel pile.

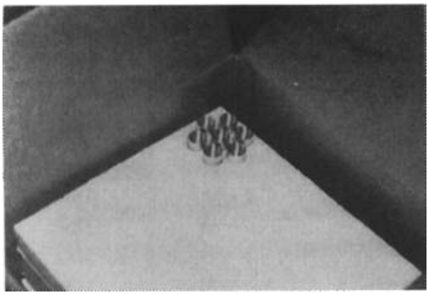


Fig 5. 39 Inside the package in external fire test

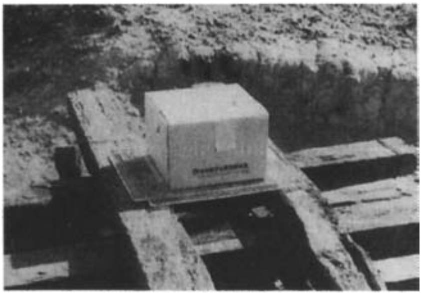


Fig 5. 40 Sample and fuel in external fire test

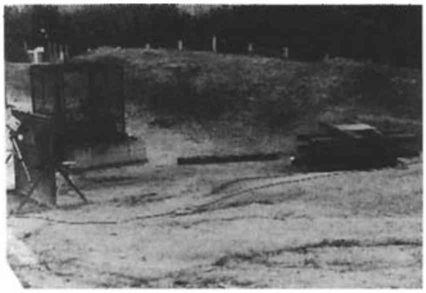


Fig 5. 41 Test point and noise detect point

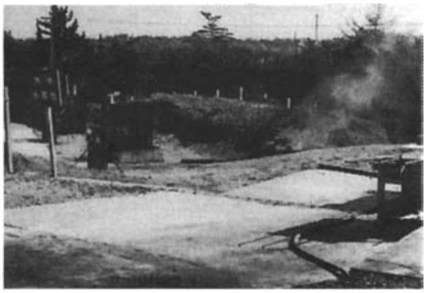


Fig 5. 42 Photo of external fire test

If the wooden fuel is too thin, it burns down too early, causing the sample to be heated slowly which can cause a potentially dangerous reaction. If the sample is placed inside the fuel, the bottom of the sample may not be heated sufficiently.

Fig. 5.41 shows the positions of the specimen fire and the noise measuring microphone. The distance between both positions was 5.5 m. The indication of the noisemeter was recorded with a remote control TV camera. A recorder was used to detect the ignition time of each generator.

Fig. 5.42 is a photo taken during the test. Simultaneous explosion of generators was not observed visually, and this was confirmed by the recorder which marked a peak for each generator ignition which showed the time of ignition(See Table 5.12). Six out of 21 generator samples exploded without igniting. The results of the test low that gas generators of this type in a package will not simultaneously ignite, even if the package is exposed to an external fire.

The range of dispersed exploded pieces is shown in Fig. 5.43. The criterion which decided whether or not the exploded pieces were hazardous was that if a piece of more that 25g flew more than 50m, it would be considered hazardous.

In this test, the generators were placed with the open ends upward. This could shorten the dispersion range of the exploded pieces. The results of the tests are summarized as follows:

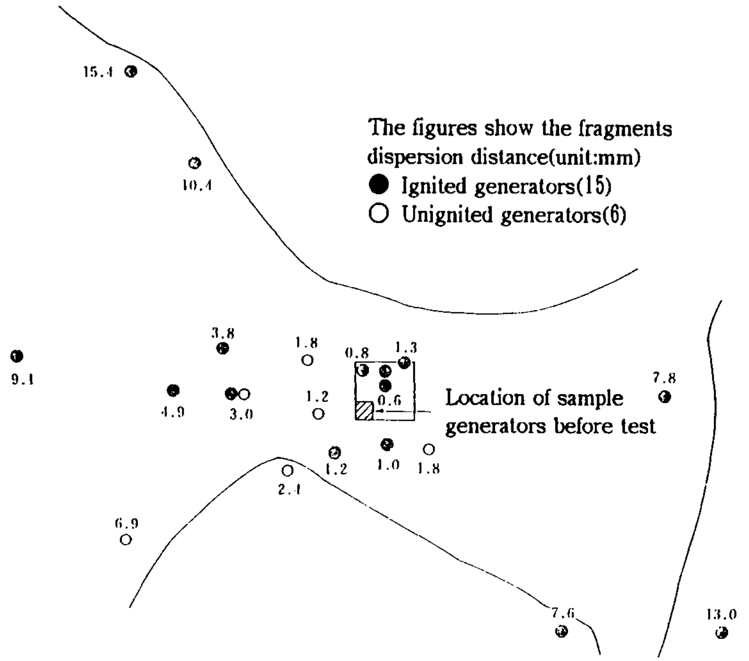

15.4
10.4
The figures show the fragments dispersion distance(unit:mm)
● Ignited generators(15)
○ Unignited generators(6)
3.8
1.8
0.8
1.3
9.1
7.8
4.9
3.0
1.2
0.6
Location of sample generators before test
1.2
1.0
1.8
2.4
6.9
7.6
13.0

Fig 5. 43 Dispersion of blasted generators after external fire test

(1) Mechanical Features

The shell of the product is machined out from an aluminum bar, and is 22mm in diameter (max. wall thickness: 5.5mm), 45.5mm in length, is cylindrical, and weighs 32 g. One end is closed tightly and the other has a plug caulked to it.

The ignition squib and gas generating compound can not be taken out unless special tools are used.

(2) Ignition Mechanism

The igniting squib can be electrically ignited but usually short circuited as well. It can not be ignited without inserting a special plug.

(3) Various Environmental Tests

The ball drop test, vibration test and heat test were carried out but at no time did any of the sample generators ignite.

(4) Ignition Test

The ignition test was carried out using samples previously used in environmental tests to compare the state of their burning to that of new samples. No difference was observed between the previously tested samples and the new ones, proving that impact, vibration, and temperature, such as imposed in these tests, will not affect the products.

Table 5.12 Ignition Time and Noise Level of Generator Samples (dB (A First))

IGNITION TIME (MIN - SEC)	NOISE LEVEL
1-54	108 dB
1-56	109
1-57	110<
1-59	110<
2-04	107
2-06	110<
2-10	110<
2-12	105
2-14	107
2-18	105
2-20	105
2-22	107
2-24	108
2-48	110<
3-32	100

(5) Fire Propagation Test

No fire propagation was observed when many sample generators were assembled connected to each other and one of them ignited. This proved that when one product accidentally ignites in group of products, the whole lot will not catch fire.

(6) External Fire Test

Assuming a package of the products is surrounded by external fire,samples of the product packaged like the actual one were brought into a fire and kept there. Simultaneous explosion did not occur, the dispersion range of blasted samples (32g each) was less than 16m, and burning samples did not enhance combustion.

5.5 Safety Evaluation of HMX Added Composite Propellant 11, 12)

5.5.1 Preface

Nitramine added composite propellants are those in which ammonium perchlorate (AP) included as an oxidizer is substituted by any of the high explosives of nitramine such as HMX, or RDX. These propellants feature: (1) a high specific thrust; (2) a low flame temperature, and (3) the possibility of a low burning speed [13,14]. They are used for upper stage motors in rockets.Much research has been conducted so far, including the present studies, on composite propellants. The composite propellant which includes nitramine with a detonator could, however, have a detonation propagating feature compared to conventional composite propellants that do not contain nitramine.

Explosives that propagate detonation are listed as Class 1.1 in international transportation regulations and are subject to strict regulations for their transportation [16]. Rocket propellants are not considered exceptions. Concerning safe handling, safety evaluation tests are being conducted to determine the hazard classification for rocket propellants [17].

Suzuki, Kato, Fukuda et al. have conducted drop hammer sensitivity tests, friction sensitivity tests, and card gap tests on composite propellants that include nitramine [18]. The authors have conducted safety evaluations in cooperation with engineers from Nippon Oils and Fats Corporation to prove that no detonation propagation exist in composite propellants. We used new evaluating methods [11,12]. The outline of our study follows. As new methods were constantly being adopted for the study, our tests were conducted on trial-and-error basis. All of the tests described here are not necessary for the evaluation of the detonating feature in composite propellants.

5.5.2 Name and objective of test and sample evaluated

(1) Variable Initiator Test Using MKIII Spring Mortar
To investigate impact sensitivity of the propellant.

(2) Variable Initiator Test Using Conventional Spring Mortar
To investigate impact sensitivity using a conventional heavy spring mortar as the MKIII is not heavy enough to obtain data when the propellant explodes.

(3) Variable Sample Quantity Test Using Spring Pendulum
To investigate detonation propagation of the propellant charged in spring pendulum.

(4) In-sand Variable Sample Quantity Test Using VP-50 Pipe
To investigate detonation propagation of the propellant when buried in sand by filling the propellant with a PVC pipe having an inner diameter of 50mm and burying it in sand.

(5) Underwater Detonation Propagation Test Using VP-50 Pipe
To investigate the detonation propagation features of the propellant underwater by filling the propellant with a VP pipe having an inner diameter of 50mm and immersing it in water.

(6) Underwater 50/60 Steel Pipe Test

To investigate detonation propagation of the propellant. The composition of samples is shown in Table 3.38.

5.5.3 Test method, results, and discussion

(1) Variable Initiator Test Using MKIII Spring Mortar

The samples were made by pouring and solidifying the sample in 15ml tubes as shown in Fig. 5.44. The result was that all the samples did not explode but burned when No. 0 detonators were used. When No. 6 detonators were used, the swing exceeded 500mm and coved not be measured. Thus the test using MKIII was abandoned.

(2) Variable Initiator Test Using a Conventional Spring Motor

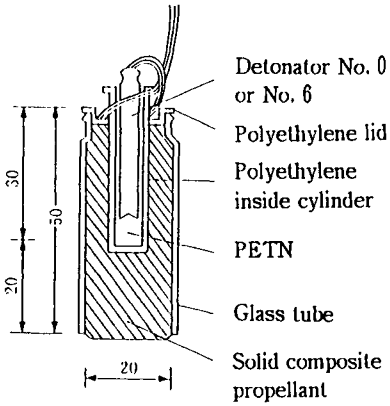


Fig 5. 44 Sample assembly for variable ignitor test of the Propellant

Because an explosion exceeding the capacity of the MKIII spring mortar was observed in the previous test, a conventional spring mortar was used instead. The conventional mortar belonged to Nippon Oils & Fats Corp., Taketoyo Works (JIS 4810 – 1978). The sample propellants were the same as those in the MKIII test, and the assembly of the samples was the same as shown in Fig. 5.44.

The results are given in Fig.3.99 through Fig. 3.101. In Fig. 3.100, the net swing angles are plotted corresponding to PETN equivalences of propellants in mortar test both with and without HME(E). According to the graph, the HMX 10% propellant is the most sensitive, followed by the 20% propellant and then the 0% propellant. However, there are two problems here. First, the net swing angle indicated here was caused by the explosive decomposition of the propellant induced by the explosion of the initiator, not by self–sustaining explosion. This fact was proved in the spring pendulum test. The difference in sensitivity indicated here could have no significant meaning.

Second, the question is whether the differences obtained in the ignitor varying tests are significant. The variety in the sample making process could have caused the differences.

Fig. 3.101 shows the results of the tests in which the addition of HMX(A) was a variable. Compared with the test results where HMX (E: fine powder) was added, the values for 10% addition and 20% addition indicate a reverse tendency. The results of these two series of tests show that the addition of 10 to 20% of HMX has little effect on impact sensitivity.

In Fig. 3.99, the comparison between propellants A, G, and H is shown. There is almost no difference between the sensitivity values measured by this method.

Excluding one exceptional case, the net swing values in the case of PETN equivalent 0.6g are larger than those of PETN equivalent 1.2g. This phenomenon has been observed in many cases where MKIII mortar is used. No explanation for this has been given so far. One hypothesis is that when an excessive quantity of initiator is supplied which is more than enough to explode, decompose, or evaporate the whole sample, the ratio of impact wave energy to whole energy is increased and is discharged into the mortar, thus the energy for expanding decreases. A series of tests is needed to prove this hypothesis.

(3) Result and Discussion of Variable Quantity Tests by the Spring Pendulum

As the propellants used here had very strong power when they were decomposed by explosion, we were unable to perform the variable sample quantity tests. Therefore, variable sample quantity tests were carried out using the spring pendulum.

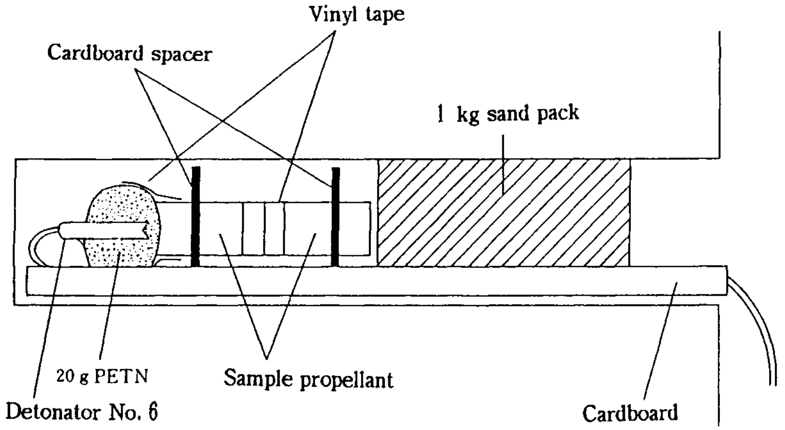


Fig 5. 45 Arrangement of the sample for variable quantity test using the spring pendulum

The samples for the test were made by solidifying propellants into portious 20mm in dia. and 50mm in length. For the initiator, 20g of powdered PETN wrapped with a thin polyethylene sheet was used in which detonator No. 6 was inserted. These were fixed with vinyl tape and positioned together with the cardboard spacer shown in Fig.5.45. A cardboard sheet was laid at the bottom so the sample would not fall out because the deep end of the mortar barrel was some what widened.

The spring pendulum used in the test was the one installed by Taketoyo Works of Nippon Oils and Fats Corp. It used a real mortar and its appearance and features are shown in Fig. 3.139.

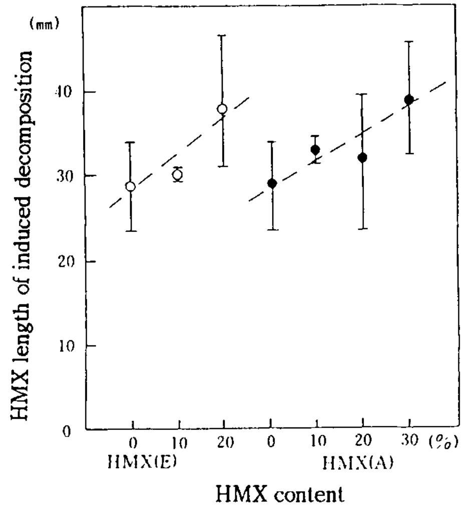


Fig 5. 46 HMX content vs. length of induced Decomposition

In the tests using the spring pendulum, propellant samples 25, 50, and 100mm long were used. In the tests using 50mm and 100mm samples, some residual material remained. In the 25mm tests, no unreacted residue was found.

Assuming the net swing of the 25mm propellant represents the actual induced decomposition of the 25mm length of propellant, the length in which induced decomposition occurs can be determined. The data thus acquired was plotted compared with the amount of HMX added in Fig.5.46. Though there are wide deviations, it showed that as the content of HMX increases, the length in which induced decomposition occurs also increases. The diameter of the sample propellant was 20mm, and the booster used for the ignitor was powdered PETN which weighed 20g. The tendency observed in the above tests has to be confirmed by tests using solid samples with a repeatable configuration and with a larger diameter. This test, however, showed that part of the results obtained by the variable ignitor test was in appearance only, and that the propellants used here may have no feature which causes self-sustaining detonation even with 1.2g of ignitor.

(4) Results and Discussion of In-sand Variable Sample Quantity Test Using VP-50 Pipe

Sample propellants were formed into a diameter of 50mm and a length of 50,100 and 150mm. To attach the booster, a hole of with a diameter of 30mm and a depth of 43mm was provided for each sample.

For the booster, 50g of the plastic explosive RDX-NG-NC (Nippon Oils & Fats No. 21) was used for each sample, having a hole of 7mm in diameter and a 20mm depth in the center to insert a detonator.

The RDX-NG-NC pellet is a high performance plastic explosive composed of 60% RDX and 40% ND added to 3% NC with an explosion speed of 7,800 m/s in a PVC pipe with a 30mm inner diameter. The same dimensions as the RDS pellet were added to it. The detonator used was the electric detonator No. 6 made by Nippon Oil & Fats. The test was carried out in the explosion test shelter in TaketoyoWorks of Nippon Oils

& Fats. The detonator was a half-cylindrical dome 2.4 m wide, 4.3 m deep and 1.5 m high, made of a steel plate. One end was open and at the other had a blower. The floor was composed of sand 1 m thick. The sample propellant was attached to the RDX booster and No. 6 detonator and buried in the sand laying horizontally at a depth of 60cm at the center of the sample. The volume of the funnel-shaped hole made by the explosion was calculated using the following formula:

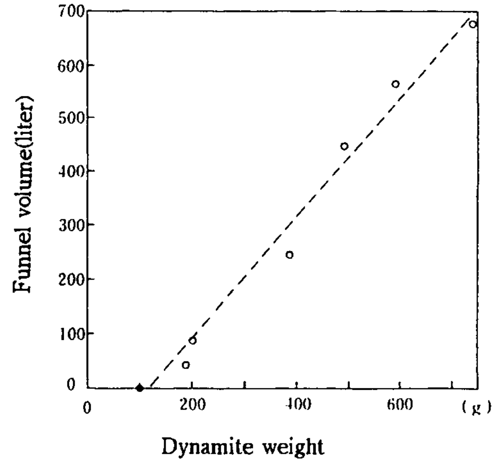


Fig 5. 47 Relationship between funnel volume and quantity of explosive in the in-sand test of Enoki No. 2 dynamite

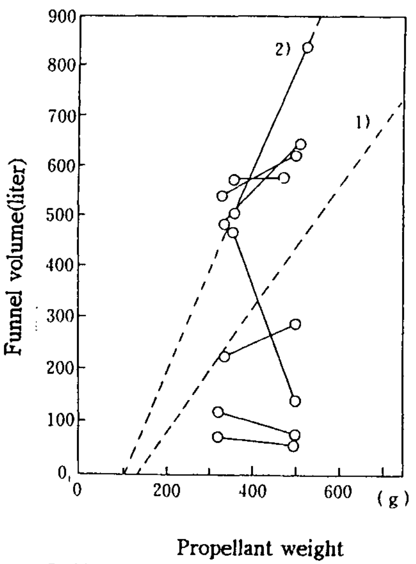


Fig 5. 48 Relationship between funnel volume and quantity of explosive in the in-sand explosion propellant
1) Line by Enoki dynamite
2) Line by propellant C

$$V = \pi abh/12$$

The test was carried out varying the quantity of propellant (variable quantity test) to investigate whether the explosion would continue when the length of sample was increased.

To understand the relationship between the amount of explosive in the VP-50 pipe and buried at a depth of 60cm and the volume of the funnel-shaped hole, another in-sand test was conducted using No. 2 Enoki dynamite. Fig. 5.47 shows the weight of the explosive (W) vs. the volume of the funnel (V). In the 100 to 740g range of explosive, V and W had a linear relationship, though no funnel was created using a 100g explosive. In the case of composite rocket propellants A to H, the results of the in-sand test are shown in Fig. 5.48. They indicate that, in the case of propellants A and H, only a small part of the sample was explodes. The exploded quantity of G (HMX 8%) was a little better than A and H, but obviously no explosion propagation occurred. In the case of D (HMX 10%), the whole sample seemed to explode when the sample was short, but only a part exploded when the sample was long. A small change in conditions seemed to cause this phenomenon when the explosion was not propagated. C (HMX (E) 20%) seemed fully propagated. If C is assumed to have propagated, B (HMX (A) 10%), C, D, E (HMX(A) 20%), and F (HMX (A) 30%) seem all fully exploded in the short samples. For long samples, however, D exploded incompletely, and with B, E, and F it was difficult to determine if they had exploded or not. Unfortunately, tests with larger quantities of samples were not allowed in this test facility.

The funnel-generating capacity of the composite propellant in an in-sand explosion is larger than that of Enoki dynamite No.2. The quantity of sample explosive in the test shown in Fig.5.48 is the sum of the composite propellant and the RDX 50g pellet, but the effect can be regarded as coming from the nature of the composite propellant because the size of the pellet is small. The ratio of dynamite to propellant in capacity can be accepted to be 1:1.6,if the inclinations of lines 1) and 2) are used for comparison.

If it is assumed that the volume of the funnel is proportional to the quantity of actually exploded propellant, the explosion factor and length of explosion for each sample can be determined by comparing the data of each sample to those of sample C, which compltely exploded.

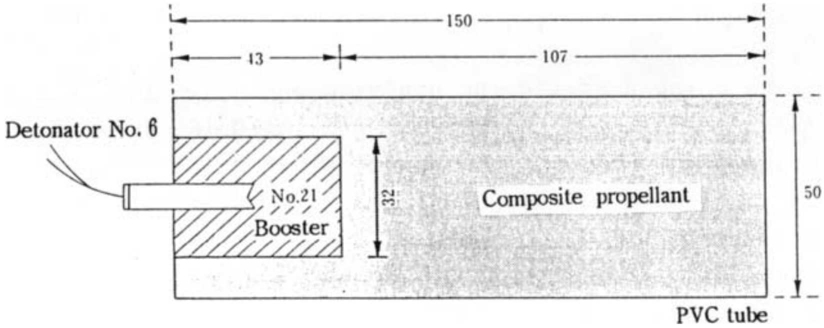


Fig. 5.49 Cross section of the propellant sample assembly used in the underwater test

(5) Result and Discussion of Underwater Test Using VP-50 Pipe

The samples used were similar to those used in the in-sand test and shown in Fig. 5.49. The test was carried out in a test pond of Taketoyo Works of Nippon Oils & Fats. The pond is 36m in diameter, with the deepest part being 10m in diameter and 8m deep. The explosion was set at a depth of 4m. When VP-50 pipe was used for the sample container, the measurement of shock wave strength and the frequency of expansion/contraction of the explosion bubble was made at 1m and 3.5m distances. The shock wave was measured with a tall marine gauge. The recording of the shock wave was made by digital memory via an amplifier. Analysis of the data was completed by a micro computer (NEC, PC 9801).

The bubble energy (E_b) and shock wave energy were calculated using the formulas below:

$$E_b = kP_0^{5/2} T_b^3 \rho_w^{-3/2}$$

Where: T = frequency of expansion/contraction of bubble
P_0 = static pressure
w = density of water
k = a constant

$$E_s = \frac{4\pi R^2}{P_w C_w} \cdot \int_0^{5\Theta} P^2 dt$$

Where: R = distance between explosion center to sensor
C_w = sound Velocity in water
Θ = damping factor of shock wave
P = pressure of shock wave

Table 5.13 Summary of Results of the Underwater Explosion Test Using VP-50 Pipe

SAMPLE	MASS	Eb	Es	ΔEb	ΔEs	ΔEb+ΔEs	ΔEs	EXPLOSION%	L LENGTH OF INDUCED EXPLOSION	ΔEb+ΔEs
No.21	50	0.108	0.0521	0.108	0.0521	0.160	0.325	100	-*	3.2(1.08)
No.21+A	441	0.231	0.0803	0.123	0.0282	0.151	0.187	7.3	<10	
No.21+B	448	0.562	0.139	0.453	0.0869	0.540	0.161	26	8-10	
No.21+C	483	1.96	0.440	1.852	0.3879	2.24	0.173	100	-*	4.64(1.57
No.21+D	489	0.334	0.103	0.226	0.0482	0.274	0.176	12.3	<10	
No.21+E	449	0.575	0.151	0.471	0.0989	0.570	0.174	27	9.4-10	
No.21+F	450	0.623	0.195	0.514	0.1429	0.657	0.218	31	14.7	
No.21+G	445	0.349	0.112	0.240	0.0599	0.300	0.200	14.4	<10	
No.21+H	434	0.217	0.0773	0.109	0.0251	0.134	0.187	6.7	<10	
No.2Enoki	200	0.445	0.144	0.445	0.144	0.589	0.244	100	-*	2.95(1.0)

*Detonation

Table 5.13 shows the summary of the results of the test. ΔE_b and ΔE_s represent the mean bubble energy and shock wave energy of the propellant; only the sum of these and the ratio of the shock wave energy to the sum are shown in the table. Also,($\Delta E_b + \Delta E_s$)/W is shown to determine whether an induced explosion occurred in the sample.

The summary shows that composite propellants of 50mm diameter and about 450g weight were not characterized by induced explosion, excluding sample C, which included 20% of the fine particle HM. The other samples showed a maximum 31% of the explosion factor (Sample F: with 30% coarse HMX).

To investigate the nature of the explosion of samples A to H, the ratio of the shock wave energy to the energy sum $\triangle E_s /(\triangle E_s + \triangle E_b)$ was plotted as shown in Fig. 5.50. The ratio for high performance explosive No. 21 is as high as 0.325, and exceed by Enoki No. 2 dynamite. Composite propellants A to H showed relatively low ratios such as 0.161 to 0.218. Even sample C, which is considered to have induced−exploded, showed a low ratio of 0.173, which was the same as other samples. The length of the exploded part of each propellant can be calculated using the explosion factor of each, assuming sample C exploded completely. A sectional view of the sample used in the underwater test is as shown in Fig. 5.49. The volume of the propellant surrounding the booster was 20% of the whole propellant. The test results indicate that, for samples A, D, G, and H, even the propellant surrounding the booster did not explode. For other samples, the length of propellant which induced explosion can be calculated.

(6) Results and Discussion of the Underwater Test
Using 50/60 Steel Pipe

When the natures of each explosive are similar to one another, an inducted explosion is more likely to occur if the diameter is larger, the explosive more tightly enclosed, and the ignition involves more energy. The BAM 50/60 steel pipe test can be used to investigate the explosion inducing feature which meets the above conditions. A 50/60 steel pipe can enclose the sample more tightly than a VP pipe.

We had not experimented underwater using a steel pipe, because we thought the measuring equipment might be damaged. Measuring by a tall marine gauge was, therefore, given up, and only frequency measuring by a microphone was used[19)] .

The propellant (400 to 460g) of was put into the 50/60 steel pipe, the void was filled with sand, and the pipe was attached to 50g of a No. 21 booster to detonate. Fig. 5.51 shows the results of plotting the bubble energy (E_b)in the steel pipe test against that of the VP pipe test (E_b°). Among the composite propellants, only sample C induced

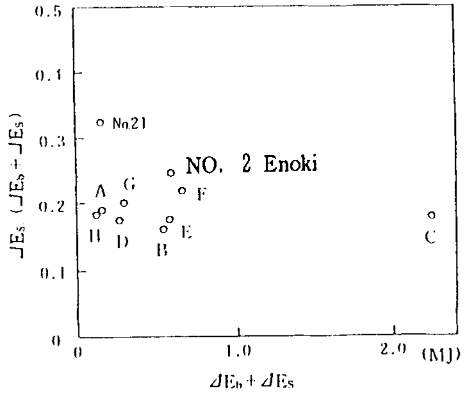


Fig 5. 50 Ratio of shock wave energy to the energy sum plotted against the sum

explosion. The bubble energy per unit radius weight for sample C was 1.60 times that of Enoki No. 2 dynamite.

A feature of the steel pipe explosion which differed from that of the VP pipe was that the bubble energy was smaller. This was shown in the dynamite test and also in that of the fully exploded sample C. One of the reasons was that a part of the explosion energy was used to break the steel pipe.

Another reason may be that the energy was also absorbed into the sand which filled the pipe.

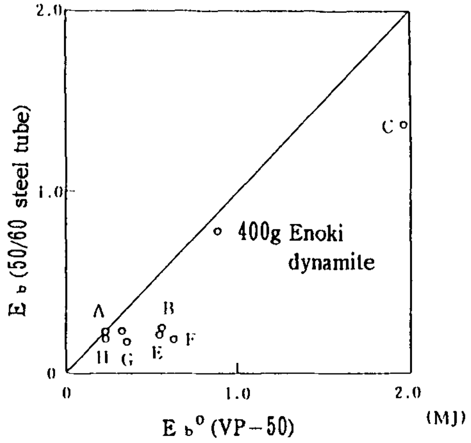


Fig 5. 51 Difference caused by containers in the underwater test of the propellant

Also differing from the case of the VP pipe, in the steel pipe test, the bubble energy of a part of the propellant which did not have an induced explosion was roughly constant for each sample (0.180 to 0.238 MJ), with no difference based on the amount of HMX observed. One explanation for this is that the increase of the explosion energy by an uninduced explosion was absorbed into the sand. This should be established by future experiments.

5.5.4 Comparison of test methods – ballistic mortar, ballistic pendulum, under–sand explosion, and underwater explosion (PCV and steel pipe)

In the variable detonator test using a ballistic mortar, all of the sample propellants (A to H) resulted in full explosions. The explosives were found at the farthest a distance of 20mm from the detonator, indicating that the sample exploded at least from a distance of 20mm. In the spring pendulum test, no induced explosion occurred in any of the samples, and the explosion distance was 26–39mm. The booster used was 20g of PETN powder and the diameter of the samples was 20mm.

In the under–sand and underwater tests, for which 50mm–diameter propellants were used, sample C detonated completety. This indicates that 20mm diameter samples cannot adequately prove if the propellant will cause induced explosion if they have larger diameters.

In the under–sand test, the range of induced explosions was fairly large. It is supposed to exceed 50mm for samples B, E and F. In the underwater test, the range of induced explosion was less than 15mm for the samples which did not explode completely in

PVC pipes, while the steel pipe test, the range was constant and nearly 0. Although these differences have not yet been experimentaly investigated, some hypotheses may be suggested.

When strong detonating energy is applied to solids which do not induce explosion, they will be pulverized. Since pulverized materials are more readily ignited than solids, it is likely that they catch fire. The explosion of such powder discharges energy which is transmitted to its surroundings.

In both underwater tests and ignition in a mortar, the amount of energy released from exploding powder is smaller, while in the in−sand explosion, the pulverized material is likely to explode before it is discharged outwardly, blasting the sand away.

With a spring pendulum mortar, the pulverized material is discharged outside the mortar before the explosion is completed. In underwater tests, complete pulverization is not likely due to the pressure of the water.

5.5.5 Conclusion

Propellants A to H do not self−sustaining explosion propagation.

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